**Naval Research Laboratory**

**Washington, DC 20375-5320**

**NRL/MR/6110--03-8704**

# Phase 1: Laboratory Investigation of Portable Instruments for Submarine Air Monitoring

THOMAS W. EVANS

*GEO-CENTERS, Inc.*
*Fort Washington, MD*

JULIANE WERNER

*Nova Research, Inc.*
*Alexandria, VA*

SUSAN L. ROSE-PEHRSSON
MARK H. HAMMOND
JOHN CALLAHAN

*Chemical Dynamics and Diagnostics Branch*
*Chemistry Division*

August 29, 2003

# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*



**1. REPORT DATE** *(DD-MM-YYYY)*
August 29, 2003

**2. REPORT TYPE**

**3. DATES COVERED** *(From - To)*
October 2002 to May 2003

**4. TITLE AND SUBTITLE**

Phase 1: Laboratory Investigation of Portable Instruments for Submarine Air Monitoring

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**
0602236N

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**6. AUTHOR(S)**

Thomas W. Evans,* Juliane Werner,† Susan L. Rose-Pehrsson, Mark H. Hammond, and John Callahan

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Naval Research Laboratory, Code 6110
4555 Overlook Avenue, SW
Washington, DC 20375-5320

**8. PERFORMING ORGANIZATION REPORT NUMBER**

NRL/MR/6110--03-8704

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

Naval Surface Warfare Center, Carderock Division
Code 3132
5001 S. Broad Street
Philadelphia, PA 19112-1403

**10. SPONSOR / MONITOR'S ACRONYM(S)**

**11. SPONSOR / MONITOR'S REPORT NUMBER(S)**

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for public release; distribution is unlimited.

**13. SUPPLEMENTARY NOTES**

*GEO-CENTERS, Inc., P.O. Box 441340, Fort Washington, MD 20749
†Nova Research, Inc., 1900 Elkin Street, Suite 230, Alexandria, VA 22308

**14. ABSTRACT**

The submarine atmosphere is a unique controlled and monitored environment in which sailors live and work for extended periods of time. Atmosphere monitoring is principally done with the Central Atmosphere Monitoring System, which is used to monitor life gases, permanent gases, and some trace constituents. However, 17 different detectors, primarily colorimetric (Dräger) tubes, are currently used to supplement the atmosphere analysis measurements made aboard U.S. Navy submarines. The submarine fleet has requested that these tubes be replaced with a more modern, less labor intensive measurement system. It is possible to replace many of the existing detectors with instruments that will incorporate more than one sensor at a time. This report presents an evaluation of six instruments equipped with oxygen, carbon monoxide, hydrogen sulfide, and lower explosive limit sensors for use in submarines as portable air monitors. This is the first phase of a three-phase program concerned with investigating potential detection methods to replace the Dräger tubes currently used. In this phase, the Dräger Multiwarn II and Enmet Omni are both strong candidates and demonstrated good performance. The cross sensitivity of the carbon monoxide sensor with hydrogen is a concern when monitoring the air in submarines and will need further consideration.

**15. SUBJECT TERMS**

Submarine air monitoring; Portable air analyzers; Oxygen; Carbon monoxide; Hydrogen sulfide; Lower explosive limit detection; Hydrogen cross sensitivity

| 16. SECURITY CLASSIFICATION OF: a. REPORT | b. ABSTRACT | c. THIS PAGE | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON / 19b. TELEPHONE NUMBER *(include area code)* |
|---|---|---|---|---|---|
| Unclassified | Unclassified | Unclassified | UL | 42 | Susan L. Pehrsson / (202) 767-3138 |

## CONTENTS

## PHASE 1: LABORATORY INVESTIGATION OF PORTABLE INSTRUMENTS FOR SUBMARINE AIR MONITORING

### 1.0 BACKGROUND

The submarine atmosphere is a unique controlled and monitored environment in which sailors live and work for extended periods of time. Atmosphere monitoring is principally done with the Central Atmosphere Monitoring System (CAMS), which is used to monitor life gases, permanent gases and some trace constituents. However, seventeen different detectors, primarily colorimetric (Dräger) tubes, are currently used to supplement the atmosphere analysis measurements made aboard US Navy submarines. As summarized in Table 1, there are a variety of circumstances under which these measurements must be made. In many cases, weekly measurements are required to supplement information obtained from CAMS. However, critical measurements are also made after casualty situations, such as a fire, or in drills for casualty situations. For example, carbon dioxide ($CO_2$), carbon monoxide (CO), hydrogen cyanide (HCN), and hydrogen chloride (HCl) levels must be monitored in a compartment for two hours after a fire. In gas free engineering applications, spaces are checked for CO, $CO_2$, oxygen ($O_2$), and combustible gas levels prior to entry into a space. Table 1 summarizes the Dräger tubes that are required, the situations under which they must be used, and the measurement level at which they must be employed. This requires that a supply of tubes, costing $4000 per year per submarine, be placed on board. Detector tubes have a limited shelf life, usually 2 years, and may expire before use. Most importantly, Dräger tube measurements give relatively slow response, are tedious, and require careful handling to be truly accurate. Even if used completely as specified, there is a degree of subjectivity in reading the colorimetric reactions on the tube. Consequently, there is little faith placed in the results and drills with the tubes are seldom properly conducted. The submarine fleet has requested that these tubes be replaced with a more modern, less labor intensive measurement system. Given the state of development of gas sensing instrumentation, it is possible to replace many of the existing Dräger tubes with instruments that will incorporate more than one sensor at a time. While it is unlikely that all of the existing tubes can be replaced with sensor packages in a cost effective manner, a good portion of the tubes outlined in Table 1 can be replaced.

It should be noted, however, that the submarine atmosphere is a unique environment. Simple deployment of off-the-shelf technology as direct drop-in replacements, while possible in some cases, is not advisable. For example, deployment of electrochemical sensors for CO detection will not work unless cross sensitivity for hydrogen is eliminated or compensated. Hydrogen levels aboard the submarine can vary extensively but are allowed to rise as high as 10,000 ppm. Consequently, any CO sensor with cross reactivity for hydrogen will generate false alarms when operations such as battery charging are carried out. Other considerations of note are the absence of significant

Manuscript approved August 1, 2003.

amounts of onboard storage for calibration standards and bulky equipment. Therefore sensors chosen for these applications must have long shelf lives and low drift so that constant recalibration, onboard or shore side, is not required. Finally, the replacement measuring devices must require a minimal amount of intervention by ship's force.

Table 1. Compounds Evaluated with Dräger Tubes in Submarines

| **Compound** | **90-Day limit (ppm)** | **24-hour limit (ppm)** | **1-hour emergency limit (ppm)** | **Measurement range (ppm)** | **Weekly** | **Damage Control** | **Escape and Rescue** | **Gas-free Engineering** |
|---|---|---|---|---|---|---|---|---|
| Acetone | 200 | 1000 | 6000 | 20-9000 | X | | | |
| Ammonia | 50 | 100 | 100 | 0-150 | X | | X | |
| Benzene | 1 | 2 | 50 | 0.1-75 | X | | | |
| Carbon Dioxide | 0.5% | 4% | 4% | 0.05%-6% | CAMS X | X | X | X |
| Carbon Monoxide | 20 | 50 | 400 | 2-600 | CAMS X | X | X | X |
| Chlorine | 0.1 | 0.5 | 3.0 | 0.05-4.5 | X | | X | |
| Combustible Gas | | | | 10% LEL to 25% LEL | | | | |
| Hydrocarbons | 60 $mg/m^3$ | | | 6-600 mg/m3 | X | X | | |
| Hydrochloric Acid | 0.5 | 20 | 20 | 0.05-30 | X | X | X | X |
| Hydrogen Cyanide | | | | | | X | X | |
| Monoethanolamine Ammonia | 0.5 | 3 | 50 | 0.05-75 | X | | | |
| Nitrogen Dioxide | 0.5 | 1 | 1 | 0.05-1.5 | X | | X | |
| Oxygen | 130-160 torr | 130-160 torr | 130-220 torr | 100-250 torr | CAMS X | X | X | X |
| Ozone | 0.02 | 0.1 | 1.0 | 0.005-1.5 | X | | | |
| Sulfur Dioxide | 1 | 5 | 10 | 0.1-15 | X | | X | |
| Toluene | 20 | 100 | 200 | 2-300 | X | | | |
| 1,1,1-trichloroethane | 2.5 | 10 | 25 | 0.25-37.5 | X | | | |

The technical objective of this effort was to procure, and test, in the laboratory and aboard ship, cost-effective replacements for the Dräger colorimetric tubes used for gas measurements aboard Navy submarines. In this effort, NSWC-CD/Philadelphia and

Naval Research Laboratory (NRL), in consultation with NAVSEA, established a priority list of Dräger tubes to be replaced with appropriate handheld, portable sensors, with the goal of selecting replacement sensors that will cover as many applications (e.g. weekly atmosphere analysis, casualty etc) as is practicable. Once priorities were established, candidate sensor packages were selected. The sensor packages were selected to a) address measurement priorities and appropriate measurement ranges with sufficient accuracy, precision, and long-term reliability; b) maximize the number of sensors in a given instrument to minimize the number of instruments that need to be procured; c) minimize the size and cost of the selected instruments; d) minimize the amount of calibration and replacement parts required. The test program was divided into three sections. Phase I will use instruments that can measure $O_2$, CO, hydrogen sulfide ($H_2S$), and combustibles (%LEL). Phase II will evaluate responses to $CO_2$, hydrogen cyanide (HCN), and hydrogen chloride (HCl), and broad range hydrocarbons. Phase III will evaluate sensors for nitrogen dioxide ($NO_2$), ammonia ($NH_3$), sulfur dioxide ($SO_2$), chlorine ($Cl_2$), ozone ($O_3$), and methylethanolamine (MEA). This report describes Phase I laboratory test results. NRL was responsible for tesing the sensors in the laboratory, assessing sensitivity, precision, accuracy and long-term drift of the instruments, as well as testing for cross sensitivity based on our knowledge of the submarine atmosphere.

## 2.0 INTRODUCTION

Identification, selection and procurement of equipment for testing was based on the needs described in Table 1 and the priorities identified above. Candidate instruments were selected for testing using the following initial selection criteria:

a. **Measurement range**: From 10% of the 90-day limit to 50% above the 1 hour limit
b. **Environmental:** Temperature range: 20-50 °C, relative humidity 35-95%
c. **Interferences**: Cross sensitivities between sensors will be investigated. Hydrogen inference, particularly on the CO sensor is critical in these studies.
d. **Accuracy**: Short-term accuracy; ± 10% relative over the specified measurement range, within 10 minutes of calibration. Long-term accuracy; ± 25% relative over the specified measurement range for up to 1 year after calibration
e. **Reproducibility**: ± 10% for measurements made within 10 minutes, over entire measurement range.
f. **Size**: Less than 0.5 cubic foot volume.
g. **General features**: Rugged, reliable, user friendly and field compatible, with capability to integrate several sensors into the same platform
h. **Cost:** Integrated procurement and maintenance calibration costs over the instrument lifetime not to exceed the cost of equivalent number of Dräger tubes over the same period

Six different types of portable instruments were evaluated in Phase I testing. The four originally identified and purchased are the Dräger Multiwarn II (Dräger), the Enmet Omni 4000 (Omni), the Thermo GasTech Genesis (Genesis), and the Industrial Scientific

iTX (iTX). In addition to these four instruments, an RKI Eagle (Eagle) and a Biosystems PhD5 (PhD5) were procured two months into the program. These two later instruments were not equipped with data logging capability for the first two-months of testing. For the duration of Phase I testing all instruments were configured for CO, $O_2$, $H_2S$ and combustible gases ($CH_4$, % LEL). Appendix A gives the manufacturers' specifications for each instrument evaluated.

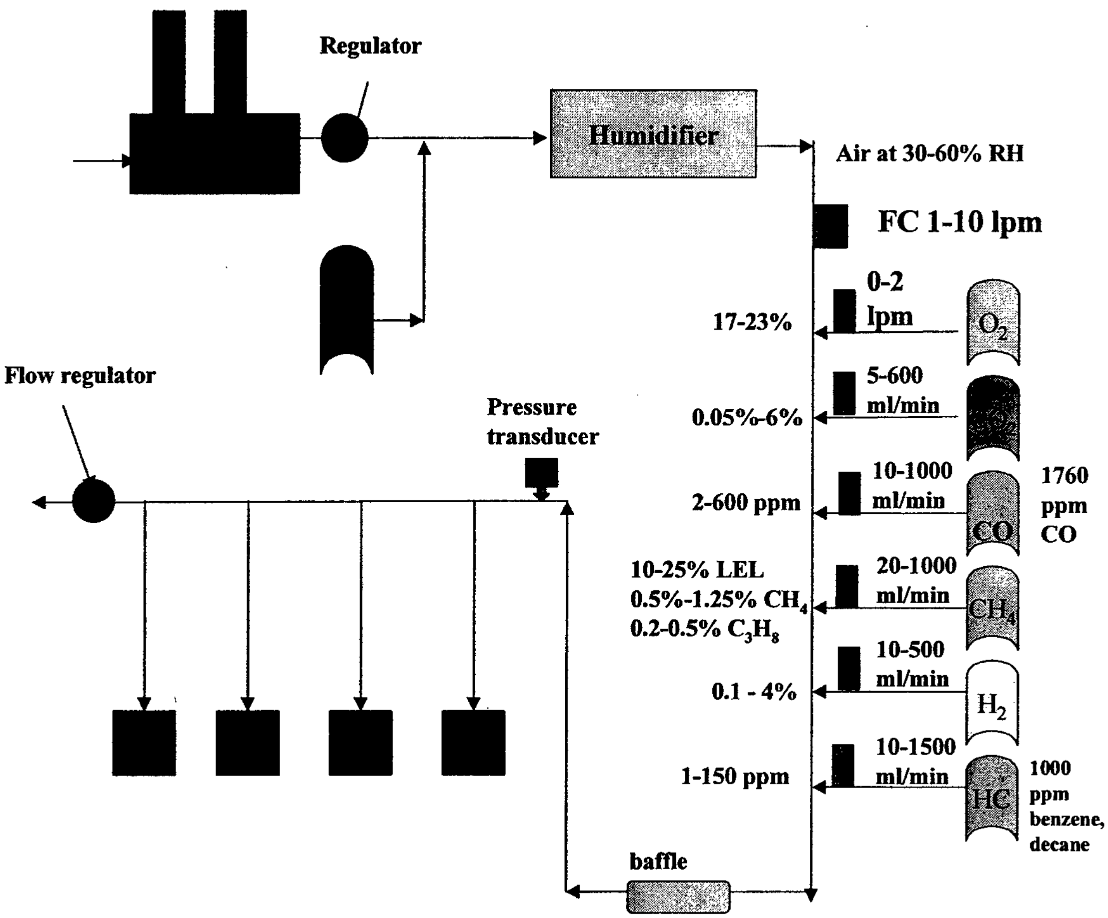
Laboratory testing was designed to assess the precision and accuracy of the portable instruments' in short-term tests (repeated over several days), in the presence of interferences, and in weekly long-term tests (up to 180 days). These tests specifically assessed the instruments' factory calibrations. For all six instruments, experiments were performed to monitor response to the following sources of interference: hydrogen, hydrocarbons, and relative humidity.

## 3.0 EXPERIMENTAL

A vapor generation system was configured using mass flow controllers and a mixing chamber to generate a known concentration in a given relative humidity (RH) air. Zero-grade air was generated by passing house-compressed air through a series of demisters to remove any oil vapors, a reciprocating dual-tower molecular sieve scrubber, a hydrocarbon trap, and finally through a Purafil canister. The air was humidified to the desired level by passing it through distilled, deionized water. A Miller-Nelson Flow Control System is used to control the temperature and humidity of the purified air. For most tests, the air was kept at approximately 25°C with 50% relative humidity. Calibrated gas cylinders are used to generate the test vapors at a given concentration. Matheson and/or Tylan Mass Flow Controllers are used to control the flow of the test gases. These gases are mixed with clean air to create a specific concentration of analyte. Each test instrument sampled the same air off the sample manifold. Figure 1 shows a diagram of the test manifold used.

The test protocol is described below. The instruments were exposed to clean, humidified air for 5-10 minutes, then the test vapor for 5-10 minutes, and finally to the clean air for 5-10 minutes. They were not exposed to another test vapor until they had fully cleared down. Instruments were re-zeroed as needed in clean air. Short-term testing was completed upon receipt of the instruments. The instruments were exposed to test vapors across the entire measurement range. The effects of relative humidity were determined by exposing the instruments to the entire range of test vapor concentrations in dry, low, medium and high levels of RH. The instruments were evaluated for cross sensitivities by exposing them to single component samples. The hydrogen cross sensitivity was thoroughly evaluated. Inference testing also included exposures to hydrocarbons. Long-term tests were conducted weekly over several months.

Two rounds of long-term testing were performed in evaluating the six Phase I portable instruments. The first round evaluated the original four instruments, and it consisted of an 82-day period. A second round of long-term testing commenced with the recalibration of the original four instruments. The PhD5 and the Eagle were included in this second round of long-term testing in order to assess the long-term performance of their factory calibrations.




FC: Flow Controller
lpm: liter per minute
ppm: parts per million
$N_2$: nitrogen
RH: relative humidity
LEL: lower explosive level

Figure 1. Test manifold designed for the instrument evaluation.

## 4.0 RESULTS

### 4.1 Short-Term Testing

Response data collected in a one to two week period following receipt of an instrument, but prior to long-term degradation of instrument performance serves as a quantitative measure of the performance of its factory calibration. The four plots below, Figures 2-5, are associated with the Genesis factory calibration. These plots are of Genesis sensor response versus applied concentration. Equations and $R^2$ values are displayed in the Figures 2-5. The Genesis is representative of the typical short-term performance of all six instruments. Perfect instrument response is that which generates a short-term performance plot with a slope of 1, an intercept of 0, and $R^2 = 1$. The results for all the instruments are given in Table 2 and the plots are provided in Appendix B. Having reviewed the short-term performance of all six instruments based on slope, intercept, and $R^2$, the instruments are rated from better to worse in this manner: Dräger, Omni, PhD5, Genesis, iTX, Eagle.

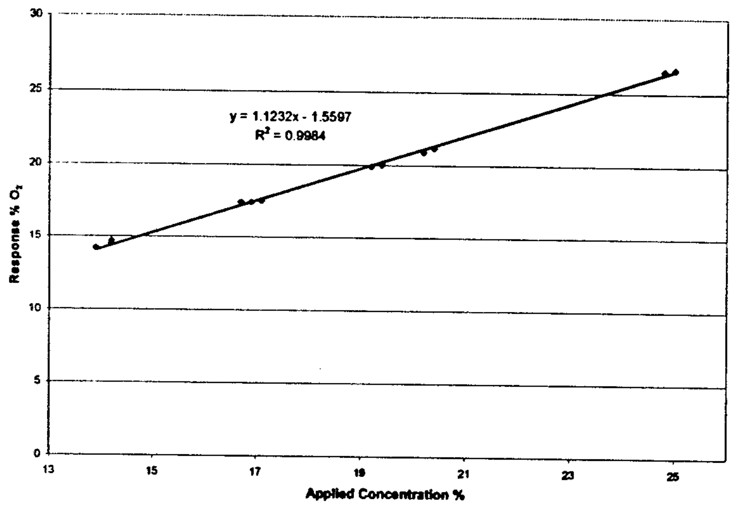



Figure 2. Genesis $O_2$ response

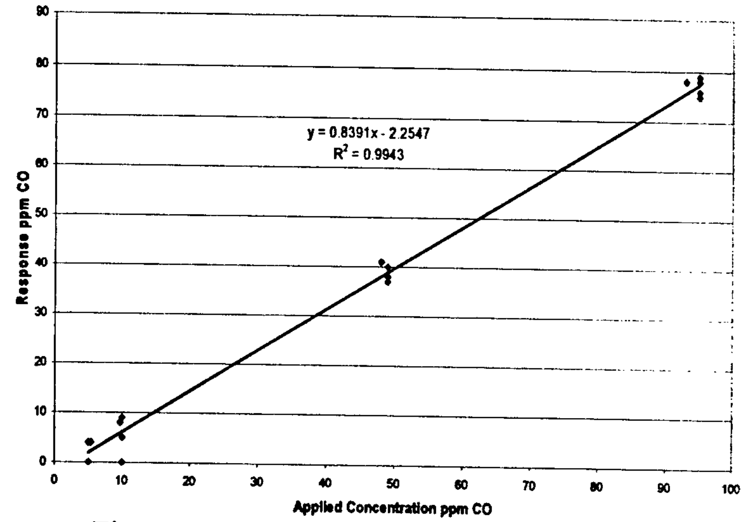



Figure 3. Genesis CO response

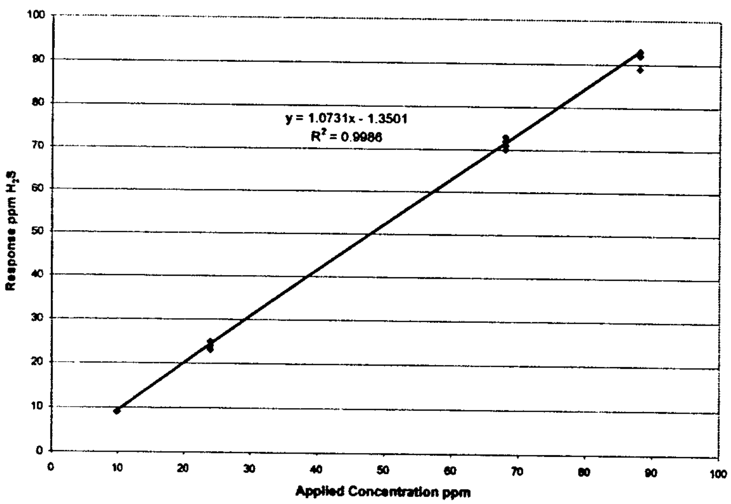



Figure 4. Genesis $H_2S$ response

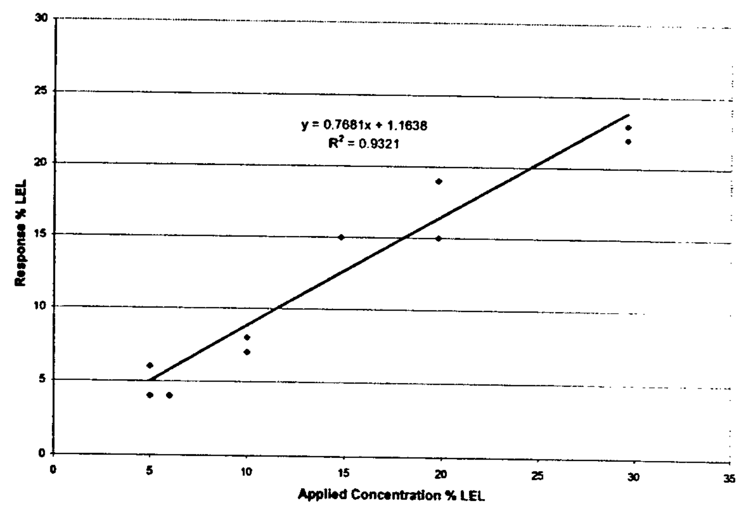



Figure 5. Genesis % LEL response

The superior short-term, factory calibration, performance of the Dräger is comparable to that of the Omni. The only significant difference between these two instruments is the $R^2$ associated with the Omni % LEL sensor is only 0.93, and all other $R^2$ values for both of these instruments' sensors are 0.99 and greater. The PhD5 and iTX factory calibrations are comparable to one another, but both perform worse than the Dräger and Omni in that their slopes vary significantly from 1, whereas Dräger and Omni slopes are all close to 1. All $R^2$ values for the PhD5 and iTX sensors are 0.99 and greater. The short-term, factory calibration, performance of the Genesis and Eagle are the worst of all six instruments. In the case of these instruments there are more substantial fluctuations in slope, intercept, and $R^2$.

**Table 2. Results of the Short-Term Calibration Tests for Each Instrument**

| **Instrument** | | **$O_2$** | **CO** | **$H_2S$** | **% LEL** |
|---|---|---|---|---|---|
| **Dräger** | **Slope** | 0.96 | 0.99 | 0.99 | 0.99 |
| | **Intercept** | 1.18 | 0.83 | -0.49 | -2.59 |
| | **$R^2$** | 0.99 | 0.99 | 0.99 | 0.99 |
| **Eagle** | **Slope** | 0.98 | 1.02 | 0.57 | 0.60 |
| | **Intercept** | 0.20 | -2.26 | 0.80 | -3.75 |
| | **$R^2$** | 0.99 | 0.99 | 0.98 | 0.96 |
| **Genesis** | **Slope** | 1.12 | 0.84 | 1.07 | 0.77 |
| | **Intercept** | -1.56 | -2.25 | -1.35 | 1.16 |
| | **$R^2$** | 0.99 | 0.99 | 0.99 | 0.93 |
| **iTX** | **Slope** | 1.16 | 1.06 | 1.12 | 2.27 |
| | **Intercept** | -2.50 | -0.59 | -1.63 | 0.88 |
| | **$R^2$** | 0.99 | 0.99 | 0.99 | 0.99 |
| **Omni** | **Slope** | 1.02 | 1.00 | 1.07 | 1.09 |
| | **Intercept** | 0.28 | 1.11 | -0.02 | 1.62 |
| | **$R^2$** | 0.99 | 0.99 | 0.99 | 0.93 |
| **PhD5** | **Slope** | 1.04 | 0.95 | 0.74 | 1.57 |
| | **Intercept** | -0.49 | -0.53 | -0.89 | 0.51 |
| | **$R^2$** | 0.99 | 0.99 | 0.99 | 0.99 |

The four original instruments were again evaluated on the basis of their short-term performance following recalibration. The results rated better to worse are: Dräger, Omni, iTX, Genesis. The post recalibration short-term performance of the iTX is only slightly superior to the Genesis. On the basis of their factory calibrations the Gensis was rated ahead of the iTX. This change in the rated order is attributed to the vastly improved performance of the iTX's % LEL sensor following recalibration.

### 4.2 Single Component Exposures

Single component exposures were performed primarily to establish any cross sensitivity among the four test gases. The observed cross sensitivities were for the Omni and Genesis CO sensors, and the PhD5's $H_2S$ sensor. Figure 6 demonstrates that early in testing the Omni CO sensor response to $H_2S$ increased over time, and then later in testing

this response stabilized at an elevated level. The large jump seen in Figure 6 between days 138 and 145 is attributed to a series of hydrogen ($H_2$) exposures, which occurred on day 142. A similar yet smaller jump is seen between days 5 and 18. This jump is attributed to a series of $H_2$ exposures, which occurred on days 9 and 10.

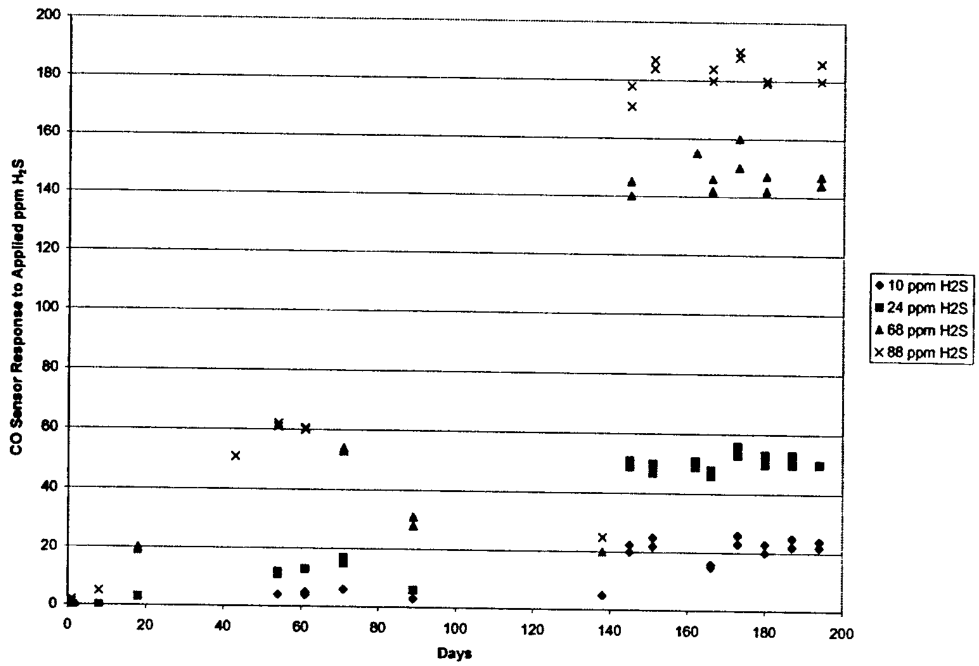



Figure 6. Omni CO Sensor Response to $H_2S$

In light of the Omni's behavior, the test gas mixtures were modified for the long-term test. In regular weekly testing $O_2$, CO, and $CH_4$ were applied to the instruments simultaneously, and $H_2S$ was tested separately. For long-term testing all six instruments were eventually tested in this manner on a weekly basis. Coincidentally the PhD5 $H_2S$ sensor demonstrates cross sensitivity to CO; therefore, testing $H_2S$ separately also proves advantageous on this point. The PhD5's $H_2S$ sensor responded to 32 ppm CO and greater, and this effect was stable over time. Throughout two months of regular weekly testing at 49 ppm CO, the PhD5 maintained an 8 ppm $H_2S$ response.

The final observed cross sensitivity was the Genesis CO sensor response to $H_2S$. Prior to recalibration the Genesis CO sensor did not respond to $H_2S$. Figure 7 shows the post recalibration Genesis CO sensor response to $H_2S$. This response was substantial and very imprecise, but the effect does increase with $H_2S$ concentration.

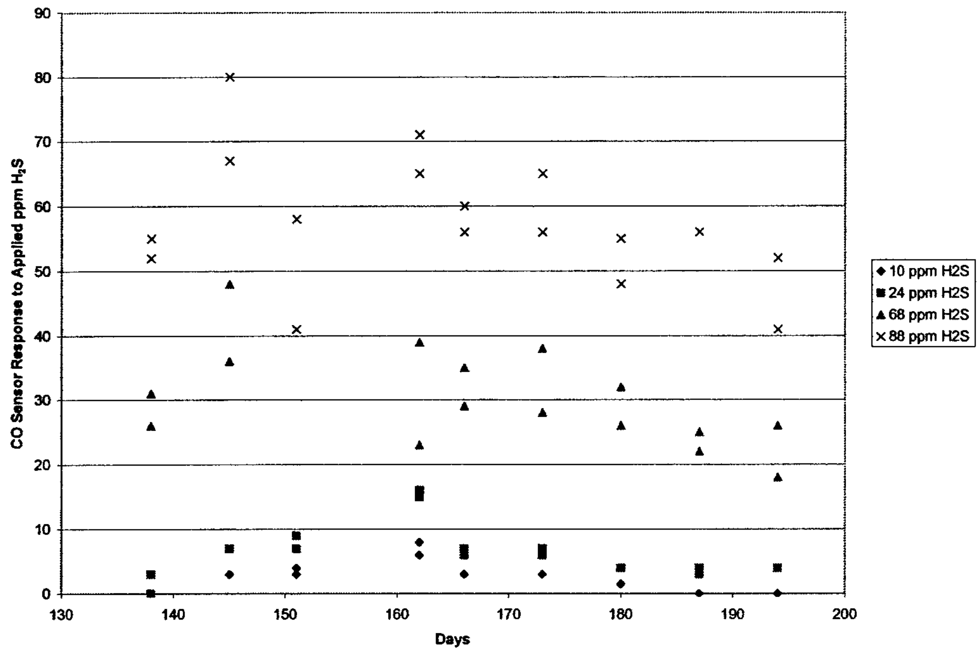



Figure 7. Genesis CO Sensor Response to $H_2S$

### 4.3 Hydrogen Cross Sensitivity

The cross sensitivity of each instrument to hydrogen ($H_2$) was tested. $H_2$ provides no response on the oxygen sensors, and any response on the combustible gas sensors is to be expected, as $H_2$ is flammable. Of most concern in these studies is the response of the CO and $H_2S$ sensors when exposed to $H_2$. All six portable instruments show CO sensitivity to $H_2$. All the instruments were evaluated twice for $H_2$ cross sensitivity.

Figure 8 summarizes the CO response for the $H_2$ interference testing to date for all instruments. The data for each instrument (response on a CO sensor for a given $H_2$ exposure) and a linear fit to the data are shown. An equation for each of the fits is shown in the plot. The response to $H_2$ increases in the following order (the best performing instrument has the lowest response to $H_2$): Eagle, iTX, PhD5, Dräger, Genesis, Omni.

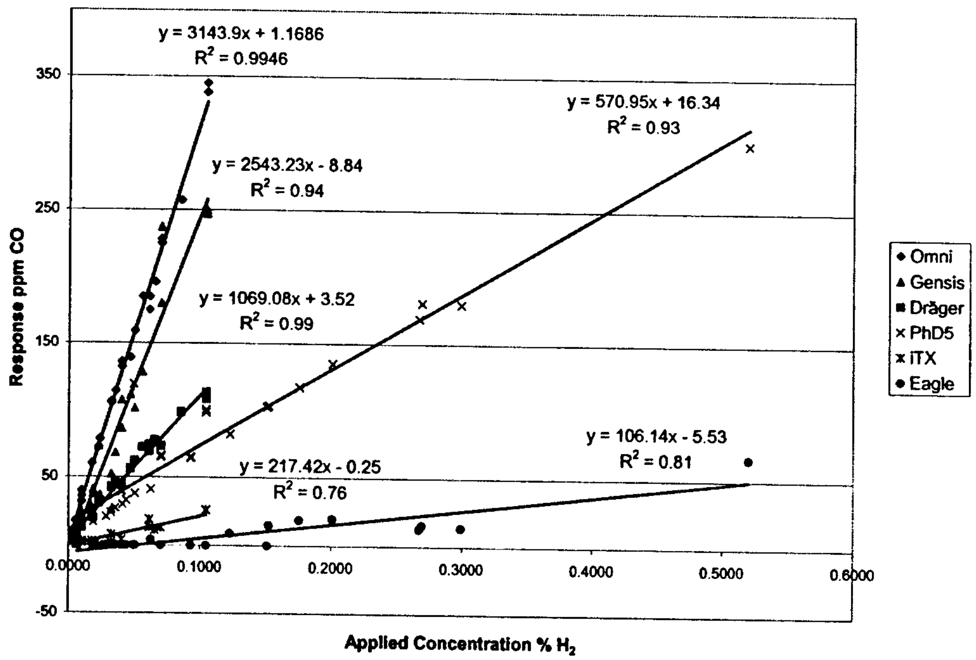



Figure 8. Response of CO sensor to $H_2$ for each instrument. Slope, intercept, and $R^2$ are displayed with each line in the plot.

The Biosystems PhD5 is one example of moderate CO response to $H_2$. With no CO present, 1000 ppm of $H_2$ (0.1%) produces a response of 60-70 ppm in the PhD5. Thus, a response of 20 ppm CO (90 day limit) would be produced by 300 ppm of $H_2$, a conservative estimate of the shipboard $H_2$ concentration. $H_2$ also induces a response in the PhD5's $H_2S$ sensor (1000 ppm $H_2$, produces a response of 20 ppm $H_2S$). The original four instruments showed no response to $H_2$ on their $H_2S$ sensors. The RKI Eagle is less sensitive to $H_2$ interferences than any of the other instruments tested. A test vapor of 1000 ppm $H_2$ produces less than 10 ppm response on the Eagle CO sensor, and the Eagle's $H_2S$ sensor shows no response to $H_2$.

The Eagle is in fact the best instrument in terms of CO/$H_2$ cross sensitivity; however, this instrument performed poorly in all other categories. The Omni and Dräger instruments are both superior instruments in terms of the measurement of CO, but both of these CO sensors are very prone to CO/$H_2$ cross sensitivity. Fortunately $H_2$ sensors were available for testing in the Dräger and the Omni instruments. These two $H_2$ sensors were tested in tandem with their respective CO sensors for their response to $H_2$, and for their cross sensitivity to CO. Various concentrations of CO were applied to the Omni and Dräger with a 100 and a 200 ppm $H_2$ background. Conversely various concentrations of $H_2$ were applied to the Omni and Dräger in the presence of 25 and 50 ppm CO background. Several concentrations of $H_2$ were also independently applied to the instruments. Figure 9 demonstrates that the Dräger $H_2$ sensor is cross sensitive to CO.

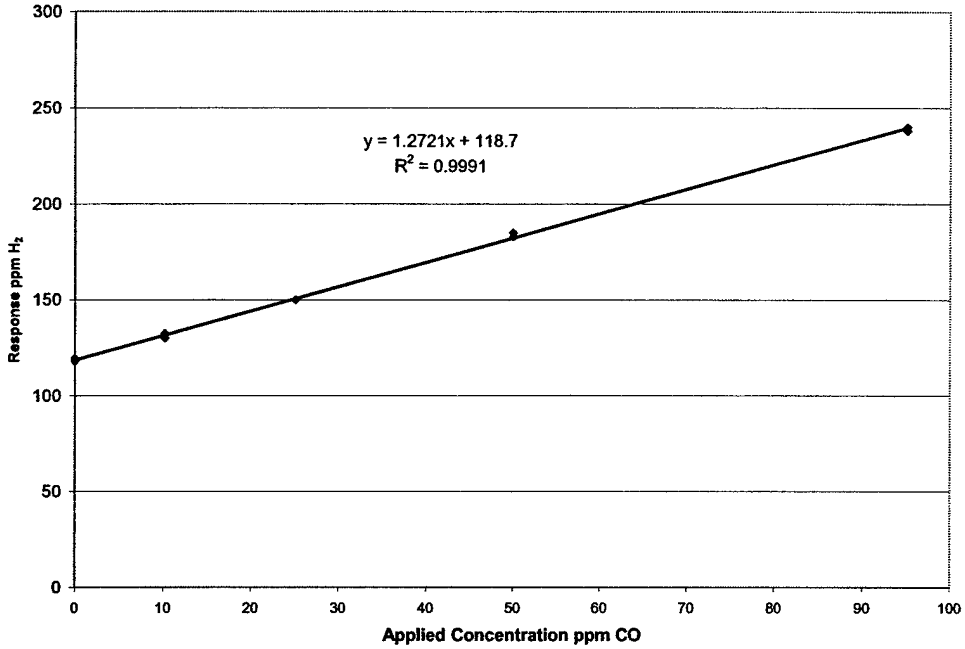



Figure 9. Dräger $H_2$ Sensor Response to CO, 100 ppm $H_2$ Background

The Dräger $H_2$ sensor response increases with CO concentration. A Dräger CO and $H_2$ sensor combination for the elimination of CO sensor is therefore more complicated. However, the responses for both sensors are linear, so the response for both chemicals could be determined by solving simultaneous equations. The Omni $H_2$ sensor response is stable regardless of CO concentration. Over a range of CO concentrations from 0 to 95 ppm CO, applied concentrations of 100 ppm $H_2$ and 200 ppm $H_2$ consistently yield Omni $H_2$ sensor response of 134 ppm and 273 ppm respectively. With an $H_2$ and a CO sensor installed simultaneously the Omni automatically subtracts $H_2$ interference from its CO sensor response. In Figure 10, normal Omni CO sensor response versus applied concentration of CO in a $H_2$ free atmosphere is compared with the same CO sensor response in a 200 ppm $H_2$ background. The responses in the presence of $H_2$ exceed the ± 25% accuracy level desired by this program.

The Omni $H_2$ sensor response is approximately 35% high and the normal Omni CO sensor response in a $H_2$ free atmosphere runs about 10% high. As expected the Omni $H_2$ compensated CO response in a 200 ppm $H_2$ backgrounds runs approximately 20% to 25% lower than the applied concentration. Adjusting the $H_2$ and CO calibrations would certainly improve the Omni's ability to compensate for the $H_2$ interference. This makes the Omni an attractive option for measuring CO in the $H_2$ laden submarine atmosphere, but for one point. As discussed in the above section on single component exposures the Omni CO sensor becomes more susceptible $H_2S$ interference after exposure to $H_2$. In a submarine a conservative estimate of the average $H_2$ concentration is approximately 300 ppm $H_2$. An Omni CO sensor/$H_2$ sensor combination would not be able to accurately measure CO in an atmosphere containing $H_2S$. Taking this into consideration a Dräger

CO sensor and an Omni $H_2$ sensor for elimination of Dräger CO sensor $H_2$ interference is the best solution to the problem.

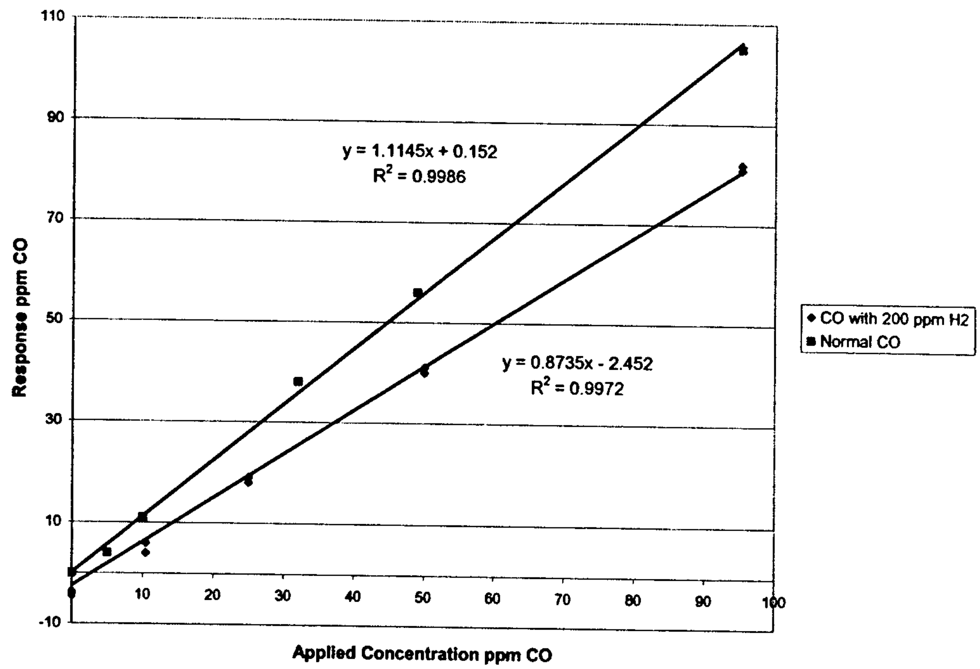



Figure 10. Normal Omni CO response compared to the Omni CO response in the presence of 200 ppm hydrogen

### 4.4 Hydrocarbon Interference Testing

A 1:1 Benzene:Octane mixture was used to evaluate the hydrocarbon interference. Hydrocarbon exposures from 2 to 105 ppm show no response other than that expected on the combustible gas sensors.

### 4.5 Humidity Testing

The first battery of humidity testing spanned 35% to 65% RH at two different concentrations for each test gas. Since the time these tests were performed, the Miller-Nelson device capable of generating relative humidity between 10% and 90% RH has been installed. Tests of all six instruments have been made to span this range of relative humidity at several concentrations of each test gas. Dry conditions (0%RH) have also been tested via exposures with dry nitrogen. These tests revealed that all of the instruments show no sensitivity to variations in relative humidity.

### 4.6 Round One, Long-Term Response Measurements

The factory calibration, long-term performance of the original four instruments was assessed in the first round of long-term testing: Dräger Multiwarn II (Dräger), Enmet Omni 4000 (Omni), Thermo GasTech Genesis (Genesis), and Industrial Scientific iTX (iTX). A period of 82 days was compiled to serve as the first round of long-term testing.

All four original instruments were recalibrated for a second round of testing. Appendix C provides the response data for all the instruments.

Unfortunately, due to a leak in the test apparatus, all data logged during a 3-week period in round two was invalid. The leak occurred in the pure $CH_4$ delivery line at the primary test gas/dilutent mixing point in the test apparatus. As a result of this leak, for the prescribed period, % LEL, CO, and $H_2S$ data are biased low, and $O_2$ data are biased high. The % LEL data are most effected, resulting in little to no % LEL sensor response between day 103 and day 124.

Logged $O_2$ levels for the prescribed period are approximately 10% higher than normal reading. The $O_2/N_2$ primary mixing point is after the $CH_4/N_2$ primary mixing point. The respective $H_2S$ and CO mixing points are before the $CH_4/N_2$ primary mixing point. Any loss in total flow at the $CH_4/N_2$ primary mixing point yields elevated $O_2$ levels. Substantial loss in total flow leaves insufficient flow for delivery to the instruments. Insufficient total flow results in further dilution of test gas mixtures with make up room air, and therefore the following observed effect: decreased CO and $H_2S$ levels, further decreased % LEL, and elevated $O_2$ levels.

A dramatic loss in % LEL sensor response occurred on day 71. This initial abrupt loss in % LEL sensor response on day 71 is attributed to the first appearance of a $CH_4/N_2$ primary mixing point leak. This minor leak then persisted and caused a continued loss in % LEL sensor response. Despite the fact that the leak began on day 71, it did not cause a measurable increase in $O_2$ sensor responses until day 103. Elevated $O_2$ levels then persisted until definitive repair of the leak prior to testing on day 131.

There is no apparent bias in $O_2$ sensor responses between days 71 and 103, but this alone is not enough to say that there was no CO or $H_2S$ bias between day 71 and 103. This period encompasses the end of the first round of long-term testing, day 71 to day 82. To accurately evaluate the long-term performance of the original four instruments' factory calibrations, then any $H_2S$ and CO bias between day 71 and day 82 must be eliminated.

Careful comparison of sensor data collected during the period of elevated $O_2$ levels (day 103 to day 124) with data collected following definitive repair of the leak provides a means to measure the extent of the CO and $H_2S$ biases during the period of elevated levels of $O_2$. Since $O_2$ levels were not elevated between day 71 and day 103, it is safe to assume that the leak, which was occurring in this period, was not as severe as the leak, which was occurring between days 103 and 124. In addition, the calibration failures for the CO and $H_2S$ sensors occurred prior to day 71.

It is noted that recalibration did occur on day 82 during the period in which $H_2S$ and CO sensor biases were carefully reviewed. However, recalibration was not performed on the test apparatus. Recalibration was performed outside the normal test apparatus via single component exposures on a separate apparatus. One and a half months of data for all

sensors was collected following definitive repair of the $CH_4/N_2$ primary mixing point leak. This includes superior % LEL sensor response for all four original instruments.

### 4.6.1 Round One, Long Term Oxygen Sensor Performance

The Oxygen sensors were exposed to varying oxygen concentrations from 14-25%. Oxygen sensors provide excellent performance over all four original instruments. Figure 11 shows the long term $O_2$ sensor response for the iTX. All four instruments provide consistent values at a given concentration of $O_2$ within ± 0.2-0.4%, and the value returned by a sensor, on average, is no more than 1.5% higher than the delivered concentration.

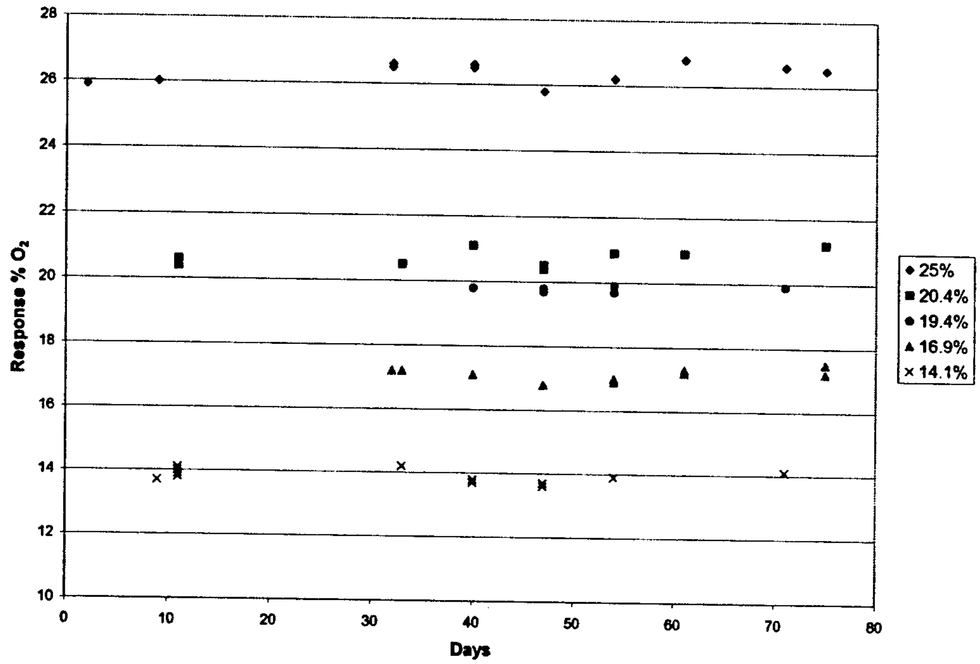



Figure 11. Round One Long-Term iTX $O_2$ Sensor Performance

The original four instruments' $O_2$ sensors tend to read somewhat high, but in most cases the sensors return a value no more than 0.6% greater than the delivered concentration. For all four instruments, the quality of the factory calibration remained the same for the full duration of the 82-day testing block. A summary of the long-term oxygen response data is provided here in Table 2. Note that the instruments are listed from top to bottom in order of best to worst performance.

Table 2. Oxygen, % by volume, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Calibration Failure |
|---|---|---|---|---|
| Enmet Omni 4000 | 14 - 25 % | +/- 0.2 % | 0.4 % high | None |
| Dräger MultiWarn II | 14 - 25 % | +/- 0.2 % | 0.6 % high | |
| Industrial Scientific iTX | 14 - 17 % | +/- 0.4 % | Accurate | |
| | 20 % | | 0.5 % high | |
| | 25 % | | 1 % high | |
| Gas Tech Genesis | 14.1 % | +/- 0.4 % | Accurate | |
| | 17 - 20 % | | 0.6 % high | |
| | 25 % | | 1.5 % high | |

4.6.2 Round One, Long Term Carbon Monoxide Sensor Performance

The factory calibration long-term performance of the original four instruments' carbon monoxide sensors, as shown below in Table 3, is nearly as good as the $O_2$ sensors. Three of the original four sensors did however falter within the 82-day, long-term testing period. The Omni performed consistently well for the entire duration of the testing period. Within the 82-day period, the other three original instruments did experience an abrupt, appreciable drop in CO sensor response at the highest two regularly applied test concentrations (49 and 95 ppm CO). In the case of the faltering instruments, a drop in sensor response is first observed at 95 ppm, and then within one to two weeks, a drop in sensor response is observed at 49 ppm CO. This serves to demonstrate that over time these sensors tend to lose sensitivity at higher concentrations first. In Figure 12, the Genesis demonstrates this behavior.

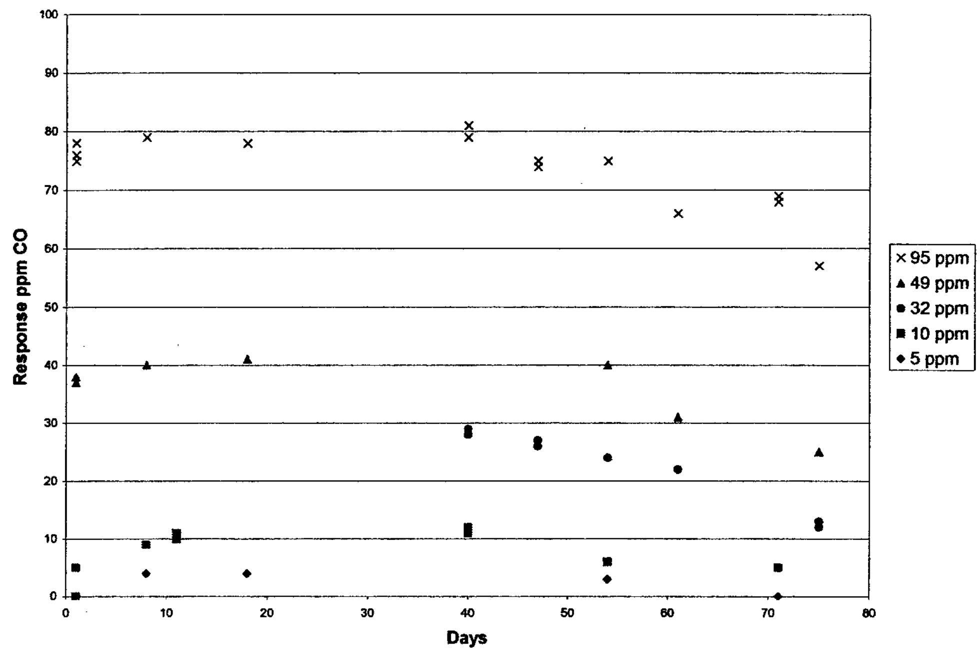



Figure 12. Round One Long-Term Genesis CO Sensor Performance

A summary of the round one, long-term CO data is provided here in Table 3. Note that the instruments are listed from top to bottom in order of best to worst performance. It is important to note that despite the Omni's superior performance in the measurement of CO, this instrument is also the worst in terms of $H_2$ cross sensitivity on its CO sensor.

Table 3. Carbon Monoxide, ppmv, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Calibration Failure |
|---|---|---|---|---|
| Enmet Omni 4000 | 0 - 95 ppm | +/- 1 ppm | Accurate | None |
| Dräger MultiWarn II | 0 - 95 ppm | +/- 1 ppm | Accurate | 7 and 6 ppm drop in response, respectively at 95 and 49 ppm, 61 days into testing |
| Industrial Scientific iTX | 0 - 95 ppm | +/- 1 ppm | 5 ppm high at 95 ppm | 8 and 6 ppm drop in response, respectively at 95 and 49 ppm, 61 days into testing |
| GasTech Gensis | 0 - 30 ppm | +/- 1 ppm | Accurate | 6 and 2 ppm drop in response, respectively at 95 and 32 ppm, 47 days into testing |
| | 50 - 95 ppm | | 10 - 15 ppm low | |

### 4.6.3 Round One, Long-Term Hydrogen Sulfide Sensor Performance

Hydrogen sulfide results for the original four instruments show a general trend toward decreased sensor response throughout the testing period, see Table 5. The iTX proves to be the worst instrument for the measurement of $H_2S$ because it shows a steady decline in instrument response over the full range of concentrations tested as shown in Figure 13.

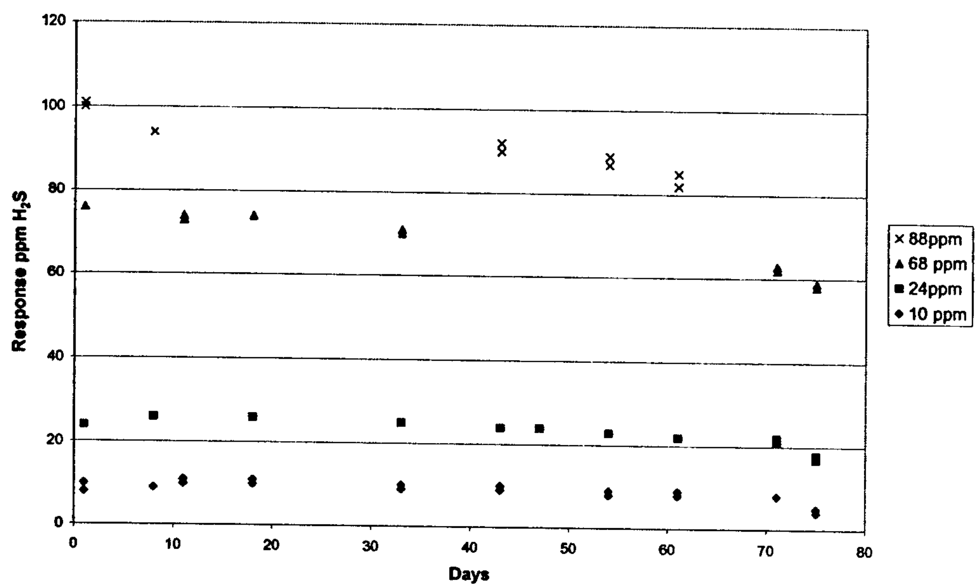



Figure 13. Round One Long Term iTX $H_2S$ Sensor Performance

The Dräger is by far the best instrument for the measurement of $H_2S$. The Dräger returns precise and accurate results over the full range of test concentrations, and failure of this instrument's calibration is delayed to 75 days. The Omni like the iTX demonstrates a steady decline in instrument response, but only at the highest applied concentration of $H_2S$ (88 ppm). The Genesis does not in fact show a steady decline in instrument response, but its factory calibration fails after only 50 days of testing. A

summary of the round one long-term $H_2S$ response data is provided in Table 5. Note that the instruments are listed from top to bottom in order of best to worst performance.

Table 4. Hydrogen Sulfide, ppmv, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Calibration Failure |
|---|---|---|---|---|
| Dräger MultiWarn II | 10 - 24 ppm | +/- 1 ppm | Accurate | 3 ppm drop in response 75 days into testing |
| | 68 - 88 ppm | +/- 2 ppm | Accurate | |
| Enmet Omni 4000 | 10 - 24 ppm | +/- 1 ppm | Accurate | 8 and 5 ppm drop in response, respectively at 88 and 68 ppm, 60 days into testing |
| | 68 ppm | +/- 3 ppm | 3 ppm high | |
| | 88 ppm | - | Shows a steady decline from (95 ppm, day 1) to (80 ppm, day 60) | |
| Gas Tech Genesis | 10 - 24 ppm | +/- 1 ppm | Accurate | 3 ppm drop in response at 88 and 68 ppm, 55 days into testing |
| | 68 - 88 ppm | +/- 3 ppm | 2 - 3 ppm high | |
| Industrial Scientific iTX | 24 ppm | - | In the first 60 days of testing response drops from 26 ppm to 22 ppm | Sensor shows a steady decline in response over the 82 days of testing prior to recalibration. Declines faster at greater concentrations |
| | 88 ppm | - | In the first 60 days of testing response drops from 100 ppm to 80 ppm | |

4.6.4 Round One, Long-Term Combustible Gases Sensor Performance

Due to the leak that occurred, the data from days 71 and 75 of testing are biased low for % LEL response. These data are not used in the analysis of the factory calibration, long-term performance of the original four instruments' % LEL sensors. For all four original instruments, the worst performing sensor is the combustible gas sensor. Each instrument shows a steady decline in $CH_4$ (% LEL) sensor response. The Genesis as seen in Figure 14 is representative of the typical % LEL sensor response. The Dräger returns the lowest sensor response over the test period. After just 40 days of testing, it fails to detect 6.8% LEL. The combustible gas sensor response for the iTX is high across the full range of % LEL tested as shown in Figure 15. At less than 17.4% LEL, the iTX reads approximately 100% higher than the applied concentration, where at greater than 17.4% LEL, it read approximately 50% higher than the applied concentration. It is clear from these results that the iTX was originally calibrated for some combustible gas other than $CH_4$. Upon recalibration, the iTX shows more accurate % LEL response than the Dräger. The Omni shows the best performance of the four original instruments; however, its performance is not substantially better than the other three instruments tested in this round of long term experiments. The information presented in Table 6 summarizes the

round one factory calibration long-term % LEL response data. Note that the instruments are listed from top to bottom in order of best to worst performance.

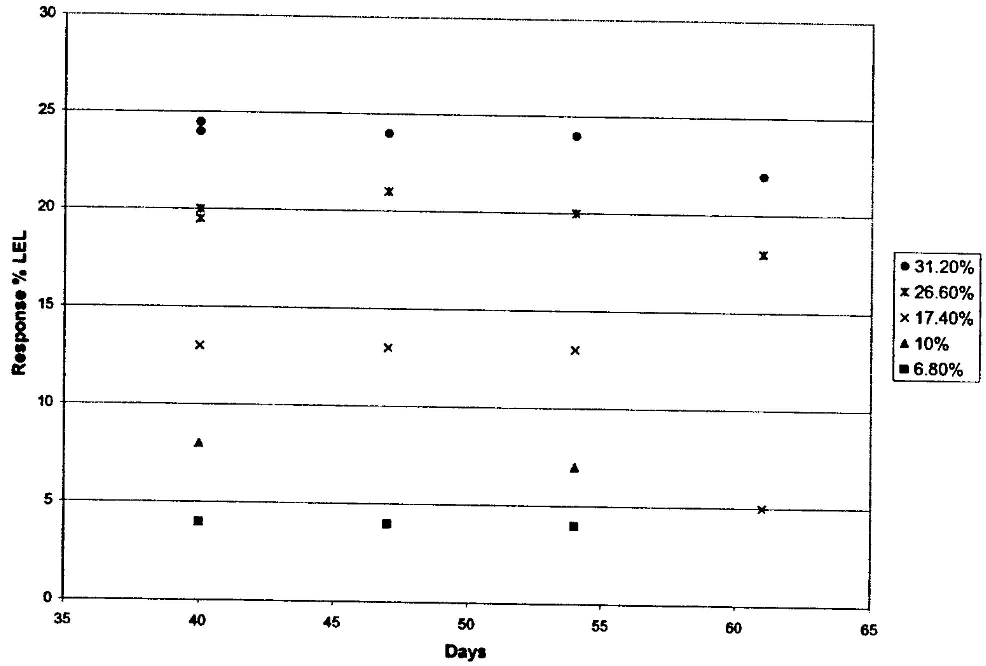



Figure 14. Round One, Long-Term Genesis % LEL Sensor Performance

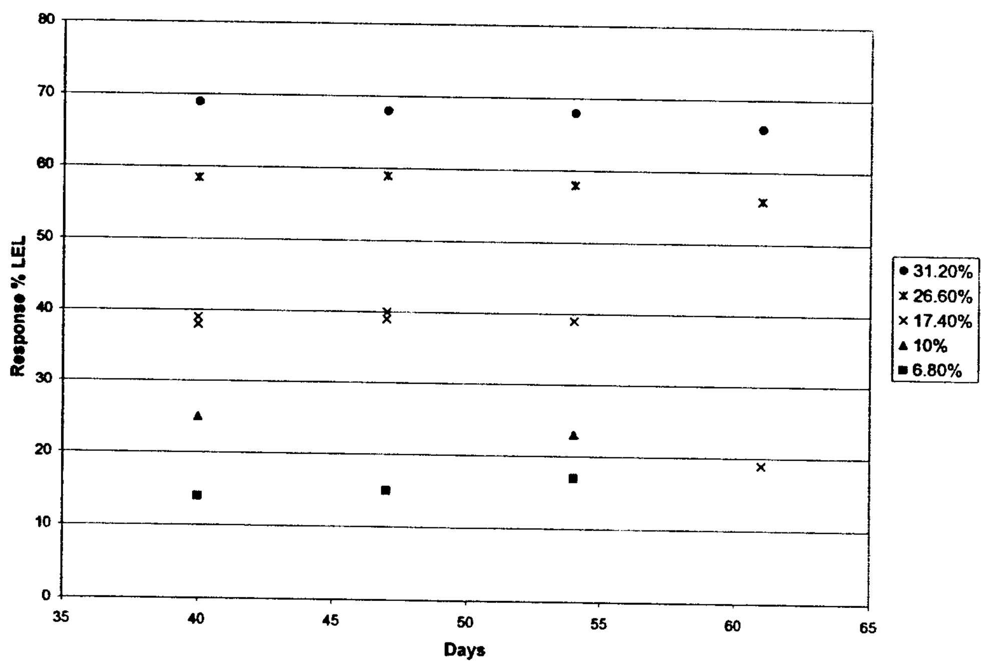



Figure 15. Round One, Long-Term iTX % LEL Sensor Performance

Table 5. Methane, % LEL, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Calibration Failure |
|---|---|---|---|---|
| Enmet Omni 4000 | 5 - 10 % | +/- 2 % | Accurate | All four instruments demonstrate a steady decline in responses at greater than 17.4 % LEL |
| | 26 - 32 % | - | * From 38 % to 36 % LEL | |
| Gas Tech Genesis | 5 % | Precise | 1 % low | |
| | 10 % | +/- 1 % | 2 % low | |
| | 26 - 32 % | - | * From 24.5 % to 22.0 % LEL | |
| Dräger MultiWarn II | 5 % | - | No detect | |
| | 10 % | +/- 2 % | 2 % low | |
| | 26 - 32 % | - | * From 25 % to 19 % LEL | |
| Industrial Scientific iTX | 5 % | +/- 3 % | 10 % high | |
| | 10 % | +/- 2 % | 10 % high | |
| | 26 - 32 % | - | * From 69 % to 66 % LEL | |

* Drop in sensor response from day 40 to day 61 at an applied concentration of 31.2 % LEL $CH_4$.

### 4.7 Round Two, Long-Term Response Measurements

Round two, long-term testing included evaluation of the post recalibration performance of the original four instruments and the factory calibration performance of the PhD5 and the Eagle instruments. Recalibration of the original four instruments occurred on day 82. Long-term testing in the second round was carried out on a weekly basis with simultaneous exposures of $O_2$, CO, $CH_4$, and separate exposures of $H_2S$. Regular weekly, round-two exposures of the original four instruments began on day 85 and proceeded until day 201, a period of 116 days. Regular weekly, round-two exposures of the PhD5 and the Eagle began on days 103 and 110, respectively and proceeded until day 201, a period of approximately 95 days. Appendix C provides the data for all six instruments.

The analysis of the round two data was performed in much the same manner as the round one analysis. Tables 6-9 below summarize the results. Within each table, all six instruments are displayed coincidentally from top to bottom in order of best to worst performing instrument. All six instruments in the second round of testing were evaluated by the same criteria. Since, regular weekly exposures of the PhD5 and Eagle began up to 25 days later than regular weekly exposures of the original four instruments, then the PhD5 and the Eagle were biased to perform better than the original four instruments. However, the PhD5 and the Eagle still performed the worst in the case of % LEL and $H_2S$. Evaluation of the $O_2$ sensors is not biased because the individual performance of each of the six $O_2$ sensors was the same throughout all testing of each instrument.

The carbon monoxide sensor performance of all six instruments tested in the second round is relatively good. The long-term performance evaluation procedure results in a simple ranked order from one to six. Even if testing of the PhD5 and Eagle had begun at

the same time as the original four instruments, the CO sensor ranks of the PhD5 and Eagle are likely to have been different by no more than one position in the resulting table. Evaluating the PhD5 and Eagle by a separate criteria is not warranted, and all six instruments' round two CO sensor results are displayed in ranked order in Table 6.

To be most consistent in evaluating the round two, long-term performance of the six instruments only data collected following definitive repair of the $CH_4/N_2$ primary mixing point leak was used. A single contiguous evaluation period of regular weekly testing is specified for each sensor. These evaluation periods are delineated in Tables 6-9. In the few instances where there is no observed difference between data collected during the period of elevated $O_2$ levels and data collected after this period, the evaluation period of that sensor is made to encompass the period of elevated levels of $O_2$. For some sensors, a change in response was observed through the course of round two. This change is reported in the Accuracy column of each table as the change from the beginning to the end of that sensors evaluation period.

### 4.7.1 Round Two, Long-Term Oxygen Sensor Performance

The oxygen sensor performance for all instruments in round two was comparable to the performance observed in round one. $O_2$ calibrations for every instrument were maintained through both rounds of long-term testing. $O_2$ sensor results are ranked in Table 6 on the basis of observed precision and accuracy of measurement in the second round of long-term testing.

Table 6. Oxygen, % by volume, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Evaluation Period |
|---|---|---|---|---|
| Dräger MultiWarn II | 14.1 - 19.4 % | +/- 0.15 % | 0.5 % high | day 138 to day 194 |
| | 20.9 - 25.0 % | Precise | Accurate | |
| Biosystems PhD5 | 14.1 % | Precise | 0.5 % high | day 138 to day 194 |
| | 16.9 % | +/- 0.1 % | 0.3 % high | |
| | 19.4 % | +/- 0.3 % | 0.6 % high | |
| | 20.9 % | +/- 0.1 % | Accurate | |
| | 25.0 % | Precise | 0.6 % high | |
| Gas Tech Genesis | 14.1 - 20.9 % | +/- 0.2 % | 0.3 % high | day 138 to day 194 |
| | 25.0 % | | 0.8 % high | |
| Industrial Scientific iTX | 14.1 - 16.9 % | +/- 0.15 % | Accurate | day 138 to day 194 |
| | 19.4 % | +/- 0.1 % | 0.3 % high | |
| | 20.9 % | | Accurate | |
| | 25.0 % | +/- 0.25 % | 1.2 % high | |
| RKI Eagle | 14.1 - 16.9 % | +/- 0.3 % | Accurate | day 131 to day 201 |
| | 19.4 % | +/- 0.6 % | | |
| | 20.9 % | +/- 0.4 % | 0.4 % low | |
| | 25.0 | | 0.2 % low | |
| Enmet Omni 4000 | 14.1 % | +/- 0.1 % | 1.0 % high | day 138 to day 201 |
| | 16.9 % | +/- 0.15 % | 0.6 % high | |
| | 19.4 % | +/- 0.2 % | 0.3 % high | |
| | 20.9 - 25.0 % | +/- 0.25 % | Accurate | |

4.7.2 Round Two, Long-Term Carbon Monoxide Sensor Performance

The Dräger instrument demonstrated good CO sensor performance in both rounds of long-term testing, and it is the best overall instrument for the measurement of CO. The second round, post recalibration, performance of the iTX instrument was better than its first round performance. The calibration remained stable, however its recalibration proved to be very inaccurate. The Omni instrument just as in the first round of testing retained a stable calibration, but it too took a poor recalibration in terms of accuracy. The Dräger demonstrated a stable and accurate recalibration. Table 7 summarizes the second round of long-term CO sensor response data. The CO sensors are ranked on the basis of their precision, accuracy, and stability of their calibrations.

Table 7. Carbon Monoxide, ppmv, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Evaluation Period |
|---|---|---|---|---|
| Dräger MultiWarn II | 5 - 49 ppm | Precise | Accurate | day 138 to day 201 |
| | 95 ppm | +/- 2 ppm | 3 ppm low | |
| Biosystems PhD5 | 5 - 10 ppm | +/- 1 ppm | 1 ppm low | day 138 to day 201 |
| | 32 - 49 ppm | +/- 1.5 ppm | 2 ppm low | |
| | 95 ppm | +/- 3 ppm | 5 ppm low | |
| RKI Eagle | 5 ppm | - | No Response | day 138 to day 201 |
| | 10 - 32 ppm | +/- 0.5 ppm | 0.5 ppm low | |
| | 49 - 95 ppm | +/- 1.5 ppm | 1 ppm low | |
| Gas Tech Genesis | 5 - 10 ppm | +/- 1.5 ppm | Accurate | day 138 to day 201 |
| | 32 ppm | +/- 2 ppm | 4 ppm high | |
| | 49 ppm | | Response Increases, 49 to 59 ppm | |
| | 95 ppm | | Response Increases, 94 to 110 ppm | |
| Enmet Omni 4000 | 5 ppm | +/- 1 ppm | Accurate | day 145 to day 201 |
| | 10 ppm | Precise | 1 ppm high | |
| | 32 - 49 ppm | | 6 ppm high | |
| | 95 ppm | +/- 3 ppm | 13 ppm high | |
| Industrial Scientific iTX | 5 ppm | Precise | 3 ppm low | day 138 to day 201 |
| | 10 ppm | | 5 ppm low | |
| | 32 ppm | | 12 ppm low | |
| | 49 ppm | +/- 1 ppm | 16 ppm low | |
| | 95 ppm | +/- 2 ppm | 32 ppm low | |

4.7.3 Round Two, Long-Term Hydrogen Sulfide Sensor Performance

The Dräger instrument demonstrated the best $H_2S$ sensor performance in both rounds of long-term testing. The $H_2S$ sensor factory calibrations on the PhD5 and the Eagle instruments are clearly inferior to the other sensors tested in round two. The PhD5 and the Eagle each showed a trend of decreased sensor response like that of the factory calibration performance of the original four sensors tested in round one. In round two, all four original instruments demonstrated the ability to maintain a stable recalibration. However, only the Dräger instrument demonstrated accuracy following recalibration. Table 8 summarizes the second round of long-term $H_2S$ sensor response data. The $H_2S$ sensors are ranked on the basis of their precision, accuracy, and stability of their calibrations.

Table 8. Hydrogen Sulfide, ppmv, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Evaluation Period |
|---|---|---|---|---|
| Dräger MultiWarn II | 10 - 24 ppm | Precise | Accurate | day 103 to 201 |
| | 68 - 88 ppm | +/- 4 ppm | 5 ppm low | |
| Industrial Scientific iTX | 10 ppm | +/- 1.5 ppm | 4 ppm low | day 103 to 201 |
| | 24 ppm | +/- 1 ppm | 8 ppm low | |
| | 68 ppm | +/- 3 ppm | 16 ppm low | |
| | 88 ppm | +/- 5 ppm | 20 ppm low | |
| Enmet Omni 4000 | 10 ppm | +/- 1.5 ppm | 4 ppm low | day 145 to 201 |
| | 24 ppm | | 8 ppm low | |
| | 68 ppm | +/- 2 ppm | 22 ppm low | |
| | 88 ppm | | | |
| Gas Tech Genesis | 10 ppm | +/- 1 ppm | 1 ppm low | day 103 to 201 |
| | 24 ppm | +/- 2 ppm | 4 ppm high | |
| | 68 ppm | +/- 12 ppm | 13 ppm high | |
| | 88 ppm | | 27 ppm high | |
| Biosystems PhD5 | 10 ppm | Precise | 4 ppm low | day 131 to 201 |
| | 24 ppm | +/- 1 ppm | 8 ppm low | |
| | 68 ppm | +/- 2 ppm | Response Decreases, 50 to 44 ppm | |
| | 88 ppm | | Response Decreases, 64 to 58 ppm | |
| RKI Eagle | 10 ppm | +/- 1 ppm | Response Decreases, 6.5 to 4.5 ppm | day 131 to 201 |
| | 24 ppm | +/- 2 ppm | Response Decreases, 16 to 12 ppm | |
| | 68 ppm | +/- 3 ppm | Response Decreases, 40 to 33 ppm | |
| | 88 ppm | +/- 4 ppm | Response Decreases, 50 to 38 ppm | |

4.7.4 Round Two, Long-Term Combustible Gas Sensor Performance

The iTX %LEL sensor performed very poorly in terms of accuracy in the first round of long-term testing, and like every other % LEL sensor tested in round one, the iTX showed a trend of decreased sensor response in time. In the second round of long-term testing, the iTX proved to be a superior instrument and it was the only instrument capable of retaining the same level of sensor response for the entire duration of the second round of testing. The Eagle, like the iTX, also demonstrated the ability to maintain its calibration, but this instrument did so with a great deal of inaccuracy and imprecision.

The Dräger and the Omni both demonstrated distinctive % LEL sensor behavior in the second round of long-term testing. The Dräger performance is seen in Figure 9. This instrument does eventually display a loss in sensor response with time, but it also shows the ability to initially maintain its calibration. The effect is most apparent at 6.8% LEL and 10.0% LEL, where the Dräger maintains stable response from day 131 to day 162. Stable responses at higher % LEL are maintained for successively shorter periods. The ability of the Dräger to initially maintain a stable % LEL sensor response allows it to be ranked ahead of the Genesis in Table 9.

Table 9. Methane, % LEL, Long Term Sensor Performance

| Instrument | Range | Precision | Accuracy | Evaluation Period |
|---|---|---|---|---|
| Industrial Scientific iTX | 6.8 % | +/- 1 % | 0.2 % high | day 138 to day 201 |
| | 10.0 % | | Accurate | |
| | 17.4 % | | 0.4 % low | |
| | 26.6 % | | 1.6 % low | |
| | 31.2 % | +/- 0.5 % | 1.6 % low | |
| Dräger MultiWarn II | See text description of this instrument's performance | | | day 131 to day 201 |
| Gas Tech Genesis | 6.8 % | +/- 1 % | Response Decreases, 7 to 4 % | day 138 to day 201 |
| | 10.0 % | | Response Decreases, 10 to 6 % | |
| | 17.4 % | | Response Decreases, 16 to 13 % | |
| | 26.6 % | | Response Decreases, 24 to 20 % | |
| | 31.2 % | | Response Decreases, 28 to 23 % | |
| Enmet Omni 4000 | See text description of this instrument's performance | | | day 131 to day 201 |
| RKI Eagle | 6.8 % | +/- 0.5 % | 5.3 % low | day 151 to day 201 |
| | 10.0 % | +/- 1 % | 7.0 % low | |
| | 17.4 % | +/- 2 % | 11.4 % low | |
| | 26.6 % | +/- 3 % | 13.6 % low | |
| | 31.2 % | +/- 5 % | 14.2 % low | |
| Biosystems PhD5 | 6.8 - 10.0 % | +/- 1.3 % | 5 % high | day 138 to day 201 |
| | 17.4 % | +/- 1 % | Response Decreases, 28 to 25 % | |
| | 26.6 % | | Response Decreases, 43 to 38 % | |
| | 31.2 % | | Response Decreases, 50 to 44 % | |

The Omni shows a moderate loss in % LEL sensor response from day 131 to day 166. Data collected on day 173 proves to be out lying data. For all six instruments on day 173, the % LEL sensor response is abnormally low. The next measurement of the % LEL sensor response occurred on day 180. As seen in Figure 16 on day 180, the Omni consistently displays a resurgence in sensor response. At the three lowest concentrations tested (6.8, 10.0, and 17.4% LEL), the Omni % LEL sensor registered responses above the applied concentration from day 180 to the end of testing. From day 180 to the end of testing for exposures to 26.6% and 31.2% LEL, the Omni sensor responses are elevated relative to previous measurement, but not above the applied concentration. On day 187, the Omni % LEL sensor registered fault and continued to register fault for the remainder of the long-term test. The Omni's peculiar behavior from day 180 to day 201 is no doubt related to this fault. The occurrence of this fault and the ensuing behavior of the Omni is the reason for its relatively poor rank in Table 9. Table 9 seen above summarizes the results of the second round of long-term % LEL sensor testing.

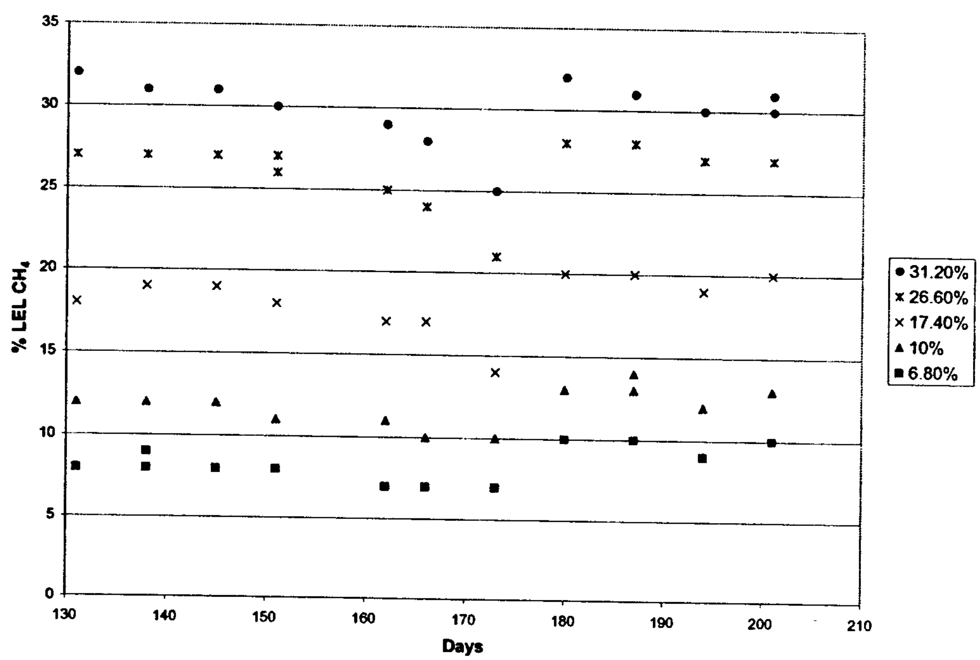



Figure 16. Round Two, Long-Term Omni % LEL Sensor Performance

### 4.8 Preliminary Field Test Results for $CO/H_2$ Cross Sensitivity

Coincident to laboratory testing shipboard submarine tests are also underway. When the instruments and logged data sheets are returned to NRL, a verification check of each instrument is performed to determine the status of its calibration following use at sea. Written records on the part of the sailors are also retained at NRL following the return of field instruments. Data and instruments have already been received from the USS Alaska and USS Maryland. Sailors performing field instrument testing also recorded field instrument standard verification checks and CAMS data from the submarines.

Preliminary review of the data shows that CO sensor response to $H_2$ on board does occur, but not to the degree expected. For the USS Alaska during the 2-month period of evaluation, the average CAMS reported concentration is approximately 275 ppm $H_2$. For this same period the average CAMS reported CO concentration is 2.8 ppm CO. Considering laboratory $H_2$ cross sensitivity testing and instrument performance (both specific to the Omni used aboard the USS Alaska) these shipboard concentrations of CO yield an expected sensor response of 58 ppm CO. The average CO response for the Omni 4000 on the USS Alaska for the same two-month period is however only 23 ppm CO. For this average to be consistent with lab results, the actual concentration of $H_2$ onboard would need to be as low as 100 ppm $H_2$. This is much lower than the reported 275 ppm $H_2$. The shipboard verification tests of the Enmet Omni 4000 tested on board the USS Alaska show that this instrument was reading an average of 43 ppm CO for a 50 ppm verification standard. This difference alone is not nearly enough to account for the large difference between the CAMS reported $H_2$ concentration (275 ppm $H_2$) and the Omni 4000 CO response of merely 23 ppm CO. Hydrogen compensated CO sensors are going to be very important for submarine analysis.

## 5.0 CONCLUSION

Following completion of Phase I analysis of the six instruments (Dräger Multiwarn II, the Enmet Omni 4000, the Thermo GasTech Genesis, the Industrial Scientific iTX, the RKI Eagle, and the Biosystems PhD5) and in considering all of the data reviewed in this report, the Dräger Multiwarn II proves to be the best overall instrument. The Enmet Omni is also a very strong candidate. These instruments are also the best candidates for Phase II at this time.

However, the CO sensor in the Dräger instrument does not compensate for hydrogen and the hydrogen sensor for this instrument also has a CO cross sensitivity. The Enmet Omni hydrogen sensor is not sensitive to CO, but the Omni CO sensor is more susceptible to $H_2S$ interference in the presence of hydrogen. Therefore, two different manufacturers are needed to provide the best solution to the $CO/H_2$ cross sensitivity problem. To accurately measure CO, an Enmet Omni 4000 should be employed with an $H_2$ sensor for subtracting $H_2$ interference on the Dräger's CO sensor.

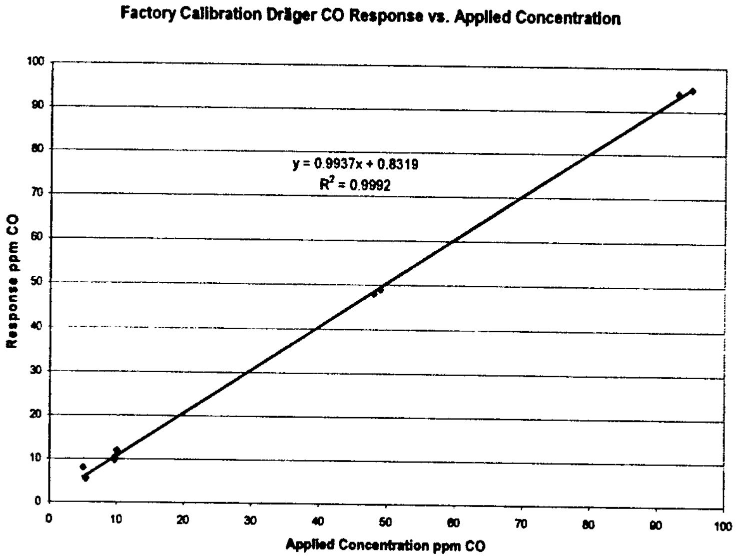
The remaining sensor ports in an Omni occupied with an $H_2$ sensor can be filled with Phase II and Phase III sensors, which test well in this instrument. Preliminary results demonstrate that the Omni broad range hydrocarbons sensor would be one positive choice for an additional sensor to be placed in this instrument. The iTX instrument has a superior % LEL sensor, and if additional Phase III sensors test well in this instrument then it could be used most efficiently. If just the % LEL sensor proves to be a positive choice for the iTX, then the Dräger % LEL sensor would suffice, but it would require more frequent recalibrating than the iTX, or alternatively sensor change out.

An overriding conclusion taken from round one long-term testing is: Phase I sensor factory calibrations, except those for $O_2$, are not guaranteed to perform well for more than two months. $O_2$ sensors perform well for more than six months. At this time it appears that the recommended calibration protocol will be on a regular bi-monthly schedule for all but the oxygen sensor. Sensor could be recalibrated off shore. Sensors could be changed out and a system established for rotating used sensors with freshly calibrated sensors for the duration of a sensors lifetime. Field verification checks with cylinders of test gas may show that after a new sensor has seen a certain amount of service in the field its subsequent calibrations may last longer than two months. This would be consistent with the increased long-term stability of the original four instruments in the second round of long-term testing following these instruments recalibrations.

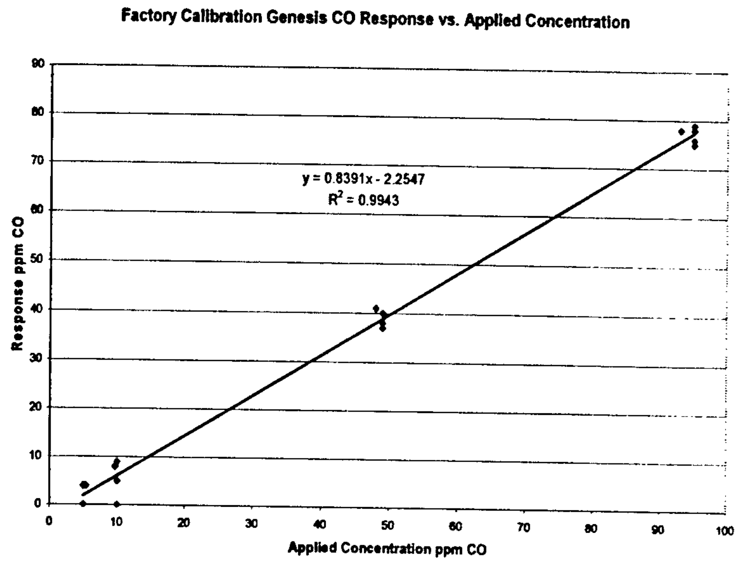
# Appendix A

| Vendor | Name of Portable Analyzer | Number of Sensors | Sensor Technology | Interchangeable Electrochemical Sensors | O2 Measurement Range | CO Measurement Range | H2S Measurement Range | Combustibles Measurement Range | Power Source | Battery Life | Durability/ Warranty | website |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Biosystems | PhD+ Portable Gas Detector | 4, with reading for 5 if Duo Tox installed | 3 electrochemical plus combustible sensor (catalytic combustion) [Oxygen required] | Yes | 0 to 30% vol. | 0 to 1000 ppm | 0 to 200 ppm | 0 to 100% LEL | NiCad or alkaline | 12 plus hours | 2 years | http://www.biosystems.com/ |
| Dräger | Multiwarn II | 5 | 3 electrochemical plus combustible sensor (catalytic combustion) plus IR sensor for $CO_2$ | Yes | 0 to 25% | 0 to 500 ppm | 0 to 100 ppm | 0 to 100% LEL | NiCad | 8 hours | 3-5 years | http://www.draeger.com/us |
| EnMet Corporation | OMNI-4000 | 4 | 3 Smart Blocks (electrochemical) plus Combustible Sensor (catalytic combustion) | Yes | 0 to 30% vol. | 0 to 1000 ppm | 0 to 100 ppm | 0 to 100% LEL | NiCad battery pack; Lithium battery for data storage | 12 -14 hours for NiCad battery; 3-5 years for lithium battery | 1 year | http://www.enmet.com |
| Industrial Scientific Corporation | iTX | 6 | catalytic combustion for combustibles; electrochemicals for all others | Yes | 0 to 30% vol. | 0 to 999 ppm | 0 to 999 ppm | 50 ppm to 100% LEL | Re-chargeable Lithium or Cell Akaline battery pack | 12 hours | 1 year | http://www.indsci.com/ |
| RKI Instruments | Eagle | 4 | catalytic combustion for combustibles; electrochemicals for all others | No | 0 to 40% | 0 to 500 ppm | 0 to 100 ppm | 0 to 100% LEL | NiCad or alkaline | 18 hours | 1 year | http://www.rkiinstruments.com/ |

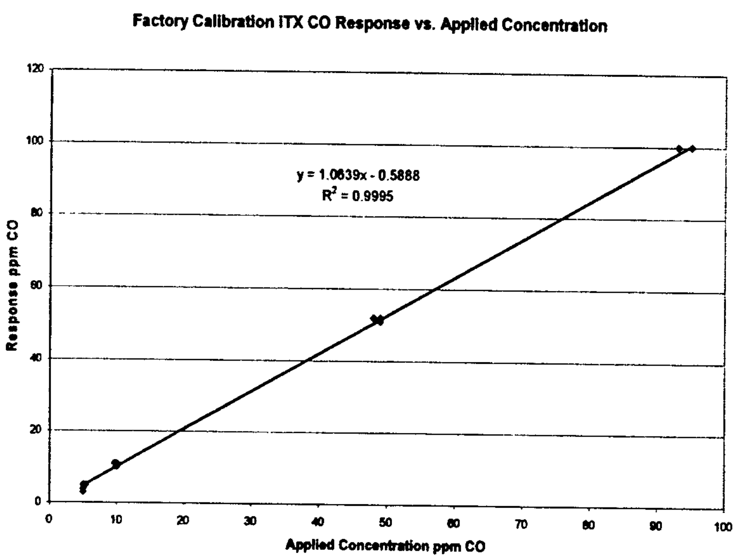
Appendix B



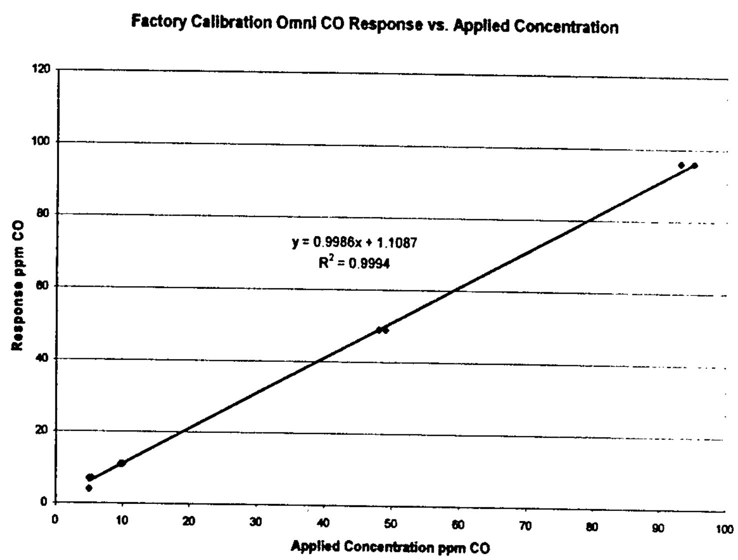
Factory Calibration Dräger CO Response vs. Applied Concentration
y = 0.9937x + 0.8319
$R^2$ = 0.9992
Response ppm CO
Applied Concentration ppm CO

Factory Calibration Genesis CO Response vs. Applied Concentration
y = 0.8391x - 2.2547
$R^2$ = 0.9943
Response ppm CO
Applied Concentration ppm CO

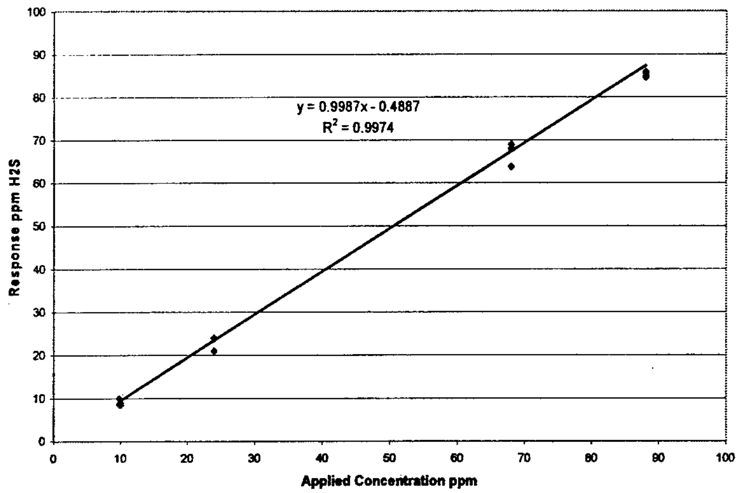



Factory Calibration ITX CO Response vs. Applied Concentration
y = 1.0639x - 0.5888
$R^2$ = 0.9995
Response ppm CO
Applied Concentration ppm CO

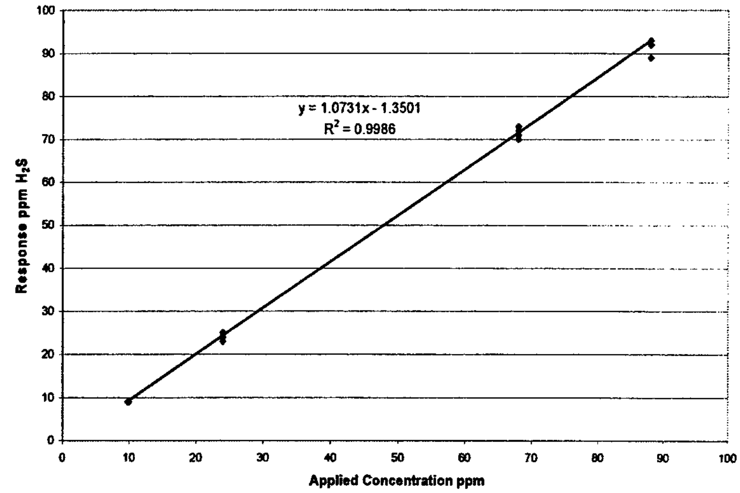



Factory Calibration Omni CO Response vs. Applied Concentration
y = 0.9986x + 1.1087
$R^2$ = 0.9994
Response ppm CO
Applied Concentration ppm CO

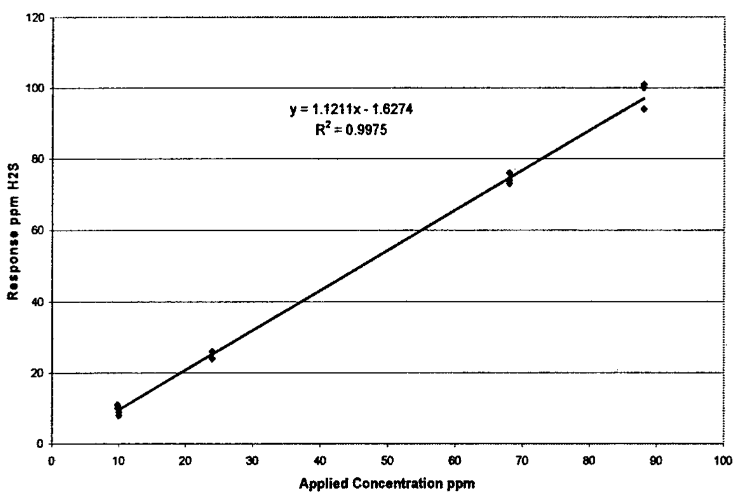
Factory Calibration Dräger $H_2S$ Response vs. Applied Concentration



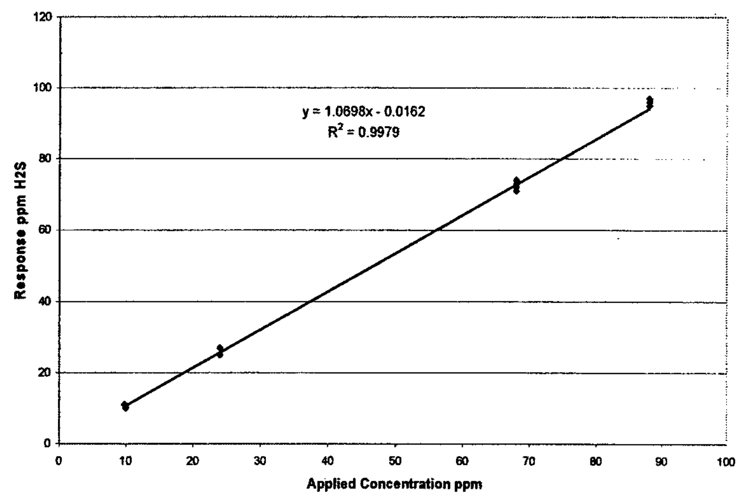

Factory Calibration Genesis $H_2S$ Response vs. Applied Concentration

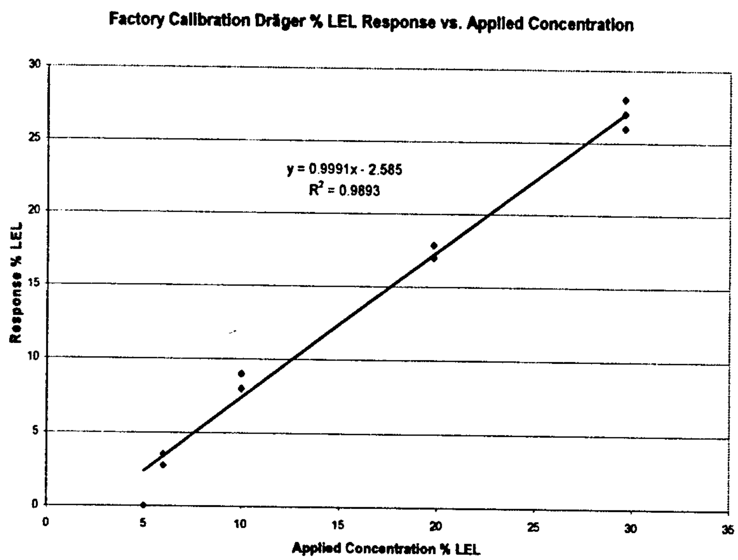


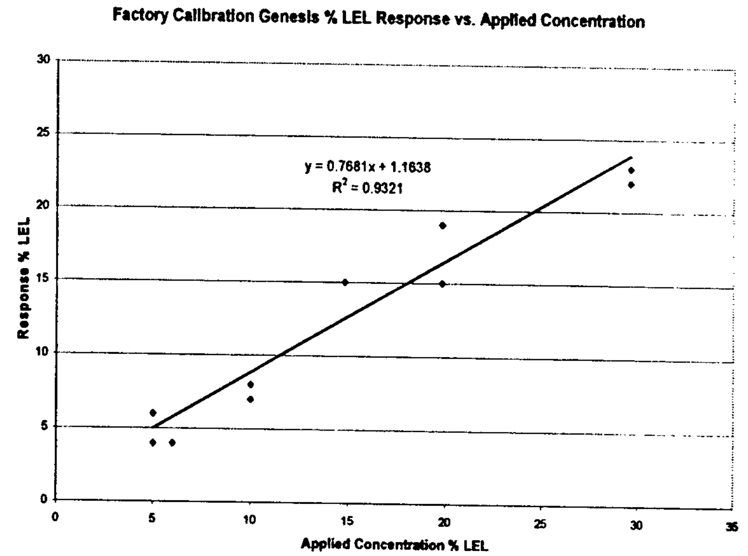

Factory Calibration ITX $H_2S$ Response vs. Applied Concentration

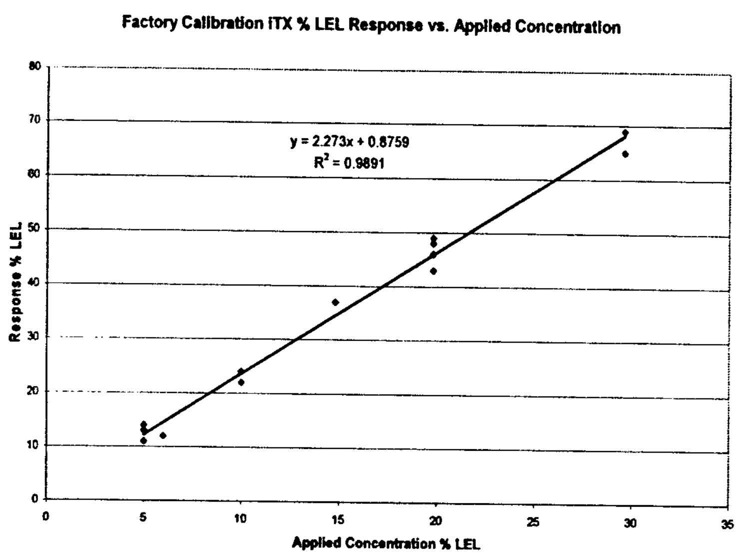


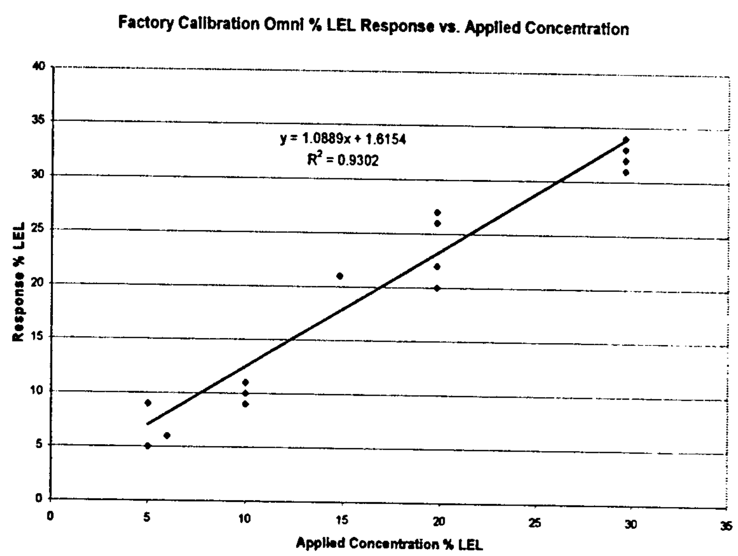

Factory Calibration Omni $H_2S$ Response vs. Applied Concentration

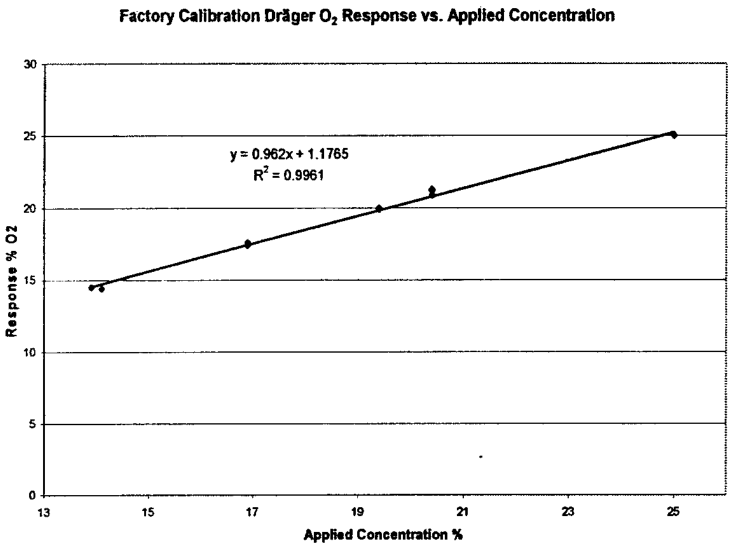



Factory Calibration Dräger % LEL Response vs. Applied Concentration
y = 0.9991x - 2.585
R^2 = 0.9893
Response % LEL
Applied Concentration % LEL

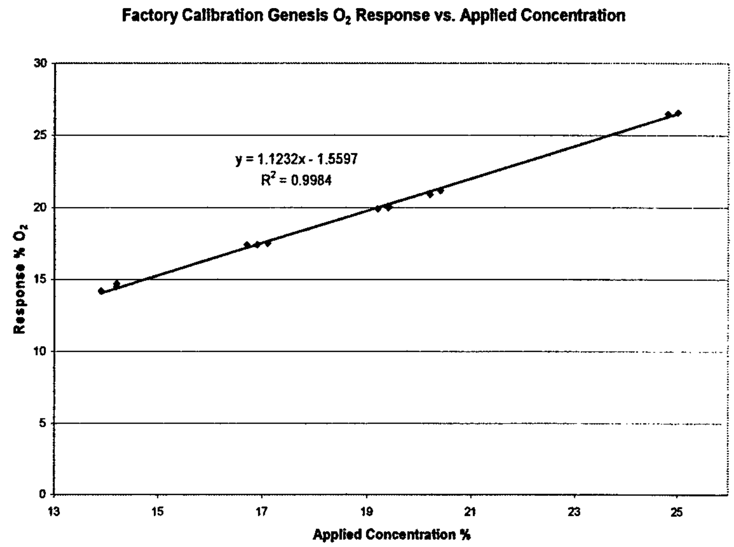

Factory Calibration Genesis % LEL Response vs. Applied Concentration
y = 0.7681x + 1.1638
R^2 = 0.9321
Response % LEL
Applied Concentration % LEL


Factory Calibration iTX % LEL Response vs. Applied Concentration
y = 2.273x + 0.8759
R^2 = 0.9891
Response % LEL
Applied Concentration % LEL

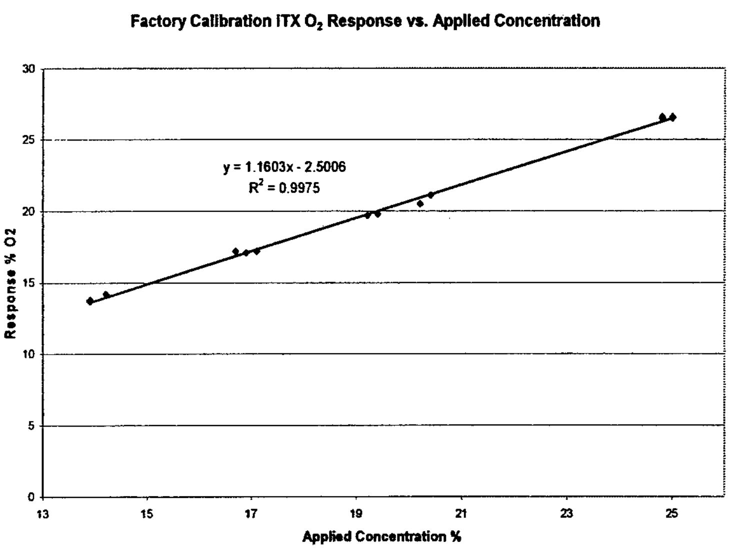

Factory Calibration Omni % LEL Response vs. Applied Concentration
y = 1.0889x + 1.6154
R^2 = 0.9302
Response % LEL
Applied Concentration % LEL



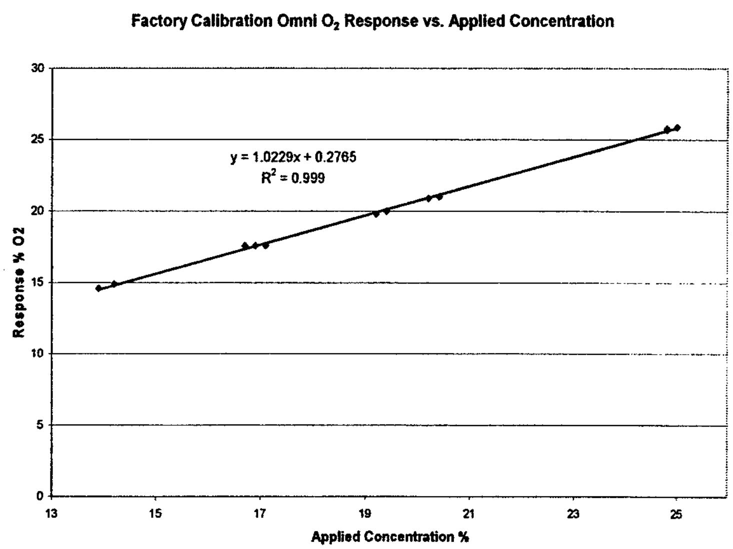
Factory Calibration Dräger $O_2$ Response vs. Applied Concentration
y = 0.962x + 1.1765
$R^2$ = 0.9961
Response % O2
Applied Concentration %

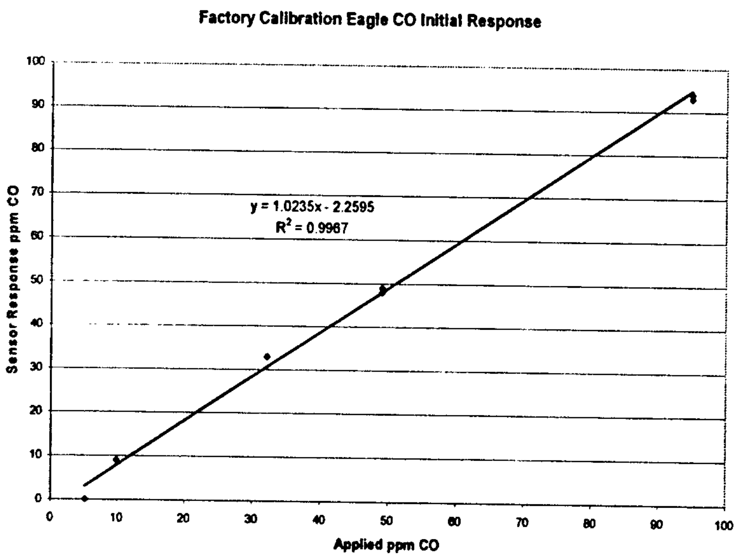
Factory Calibration Genesis $O_2$ Response vs. Applied Concentration
y = 1.1232x - 1.5597
$R^2$ = 0.9984
Response % $O_2$
Applied Concentration %

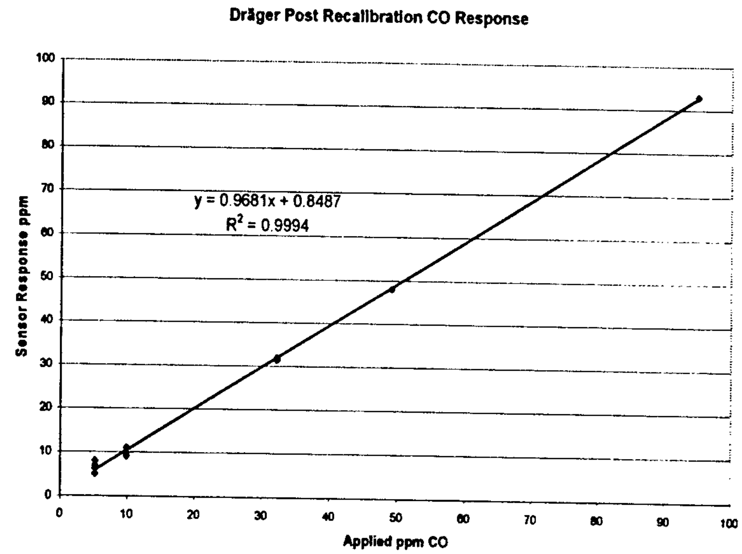



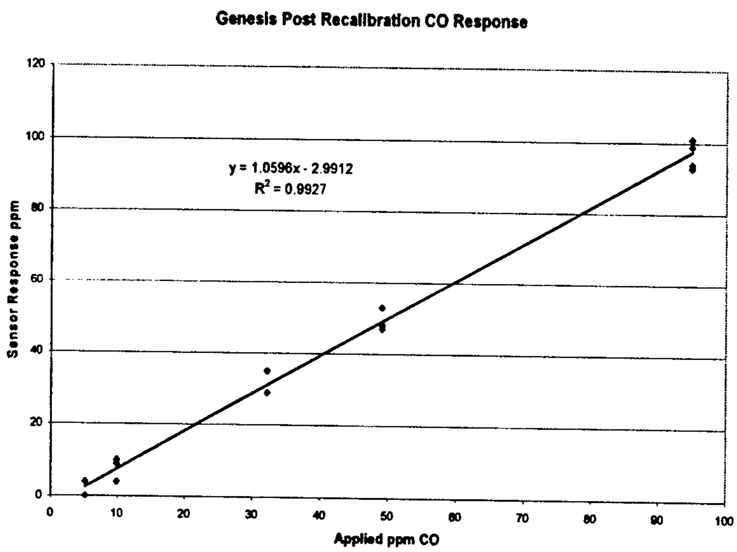
Factory Calibration ITX $O_2$ Response vs. Applied Concentration
y = 1.1603x - 2.5006
$R^2$ = 0.9975
Response % O2
Applied Concentration %

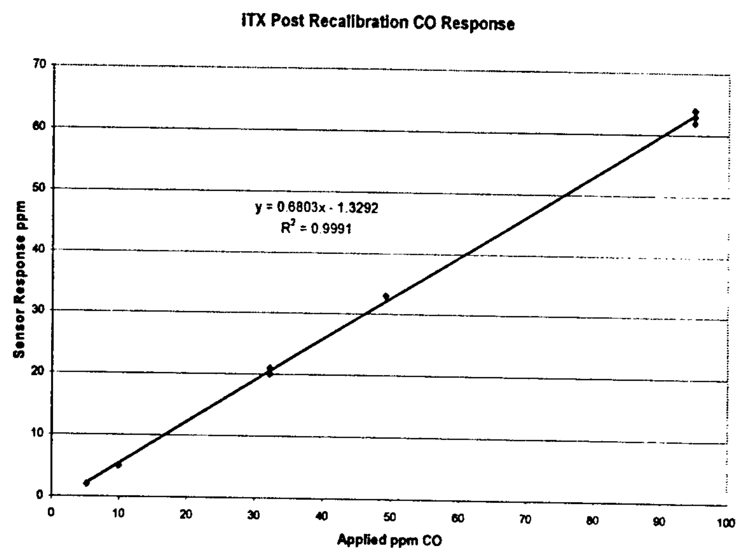



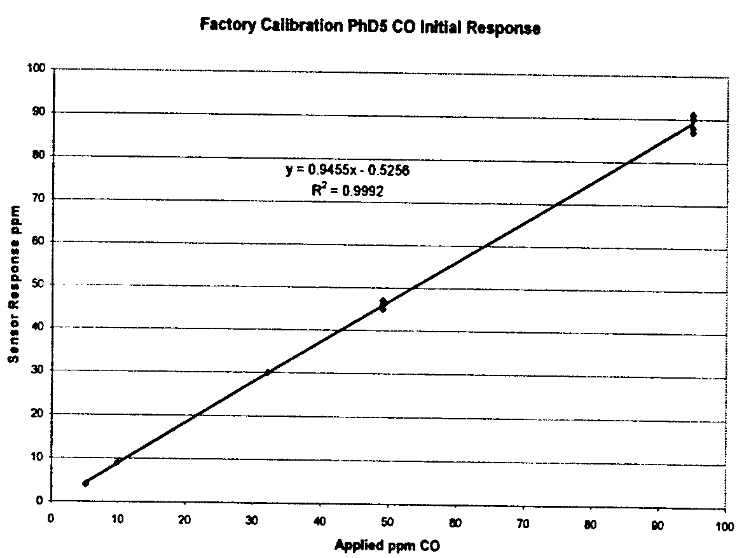
Factory Calibration Omni $O_2$ Response vs. Applied Concentration
y = 1.0229x + 0.2765
$R^2$ = 0.999
Response % O2
Applied Concentration %

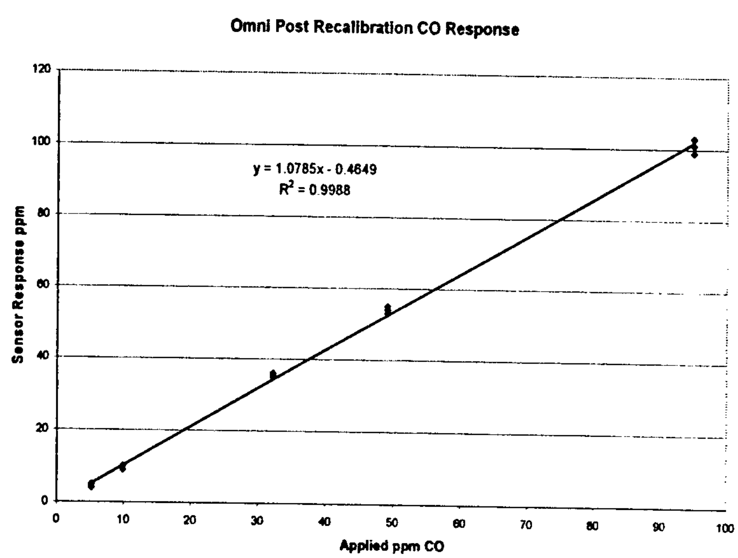

Factory Calibration Eagle CO Initial Response
y = 1.0235x - 2.2595
$R^2$ = 0.9967
Sensor Response ppm CO
Applied ppm CO

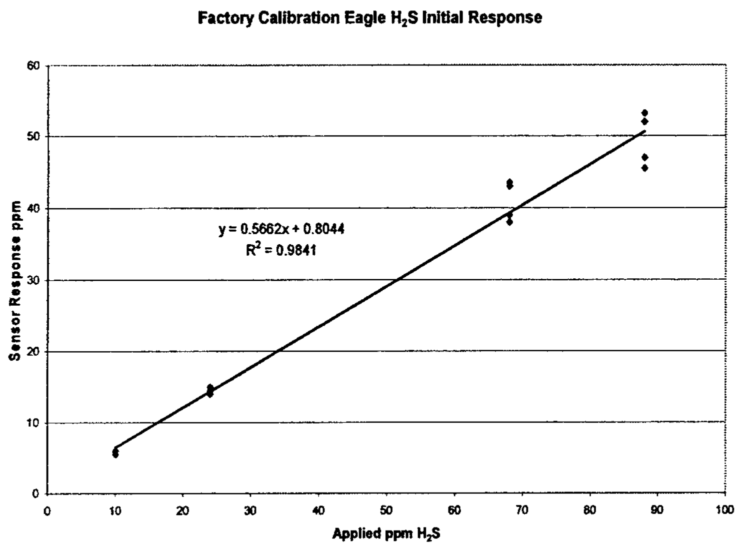

Dräger Post Recalibration CO Response
y = 0.9681x + 0.8487
$R^2$ = 0.9994
Sensor Response ppm
Applied ppm CO

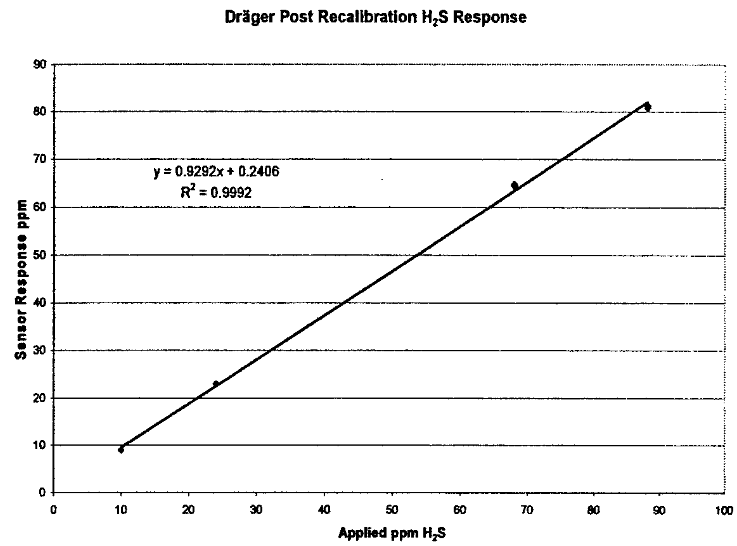

Genesis Post Recalibration CO Response
y = 1.0596x - 2.9912
$R^2$ = 0.9927
Sensor Response ppm
Applied ppm CO

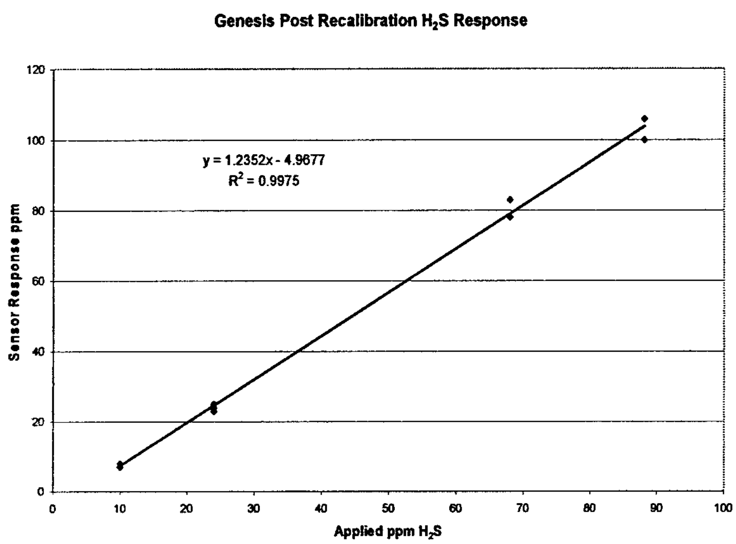

iTX Post Recalibration CO Response
y = 0.6803x - 1.3292
$R^2$ = 0.9991
Sensor Response ppm
Applied ppm CO

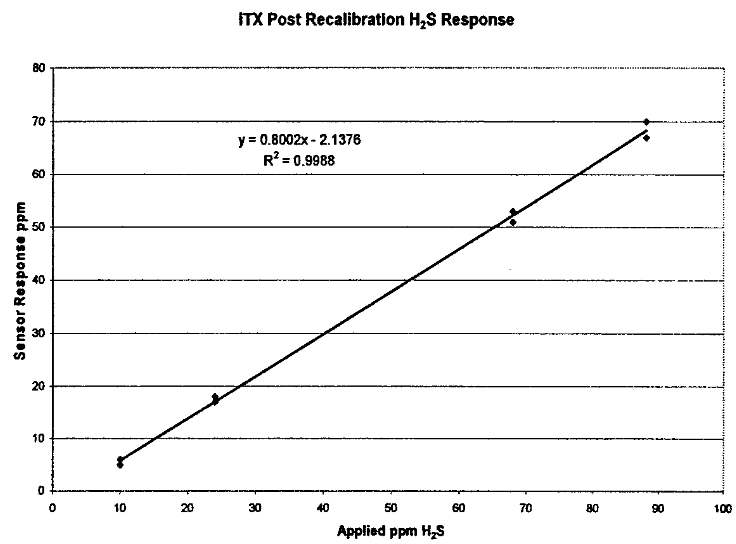

Factory Calibration PhD5 CO Initial Response
y = 0.9455x - 0.5256
$R^2$ = 0.9992
Sensor Response ppm
Applied ppm CO

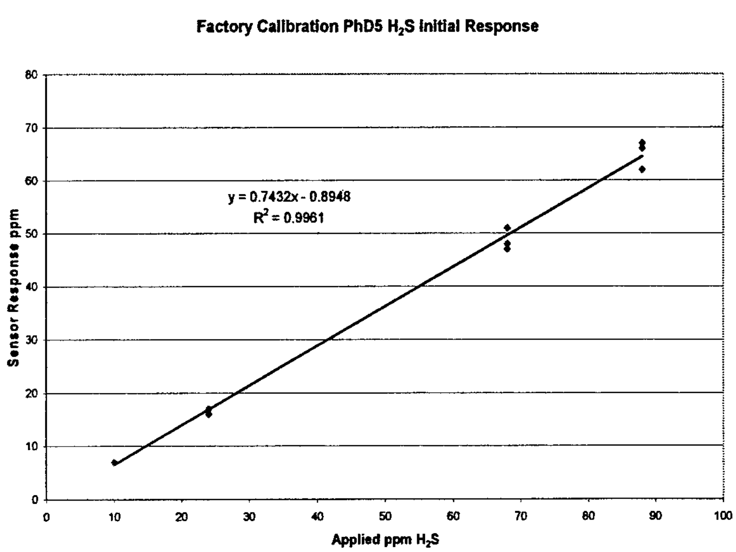

Omni Post Recalibration CO Response
y = 1.0785x - 0.4649
$R^2$ = 0.9988
Sensor Response ppm
Applied ppm CO

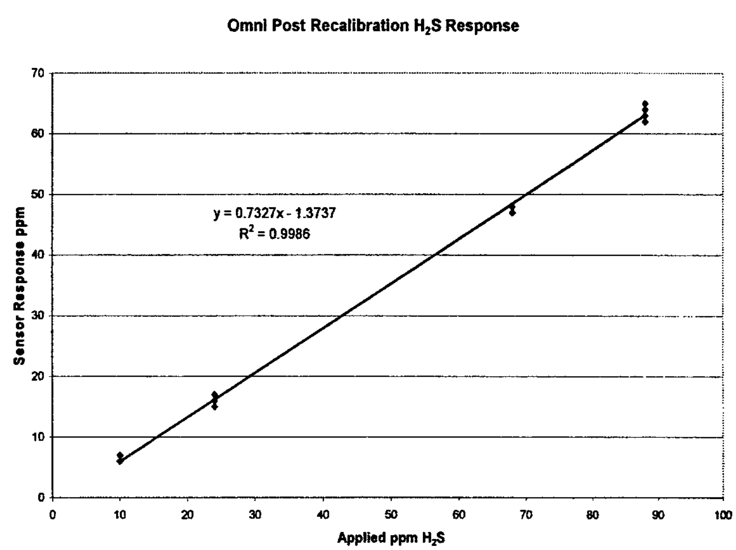

Factory Calibration Eagle $H_2S$ Initial Response
y = 0.5662x + 0.8044
$R^2$ = 0.9841
Sensor Response ppm
Applied ppm $H_2S$

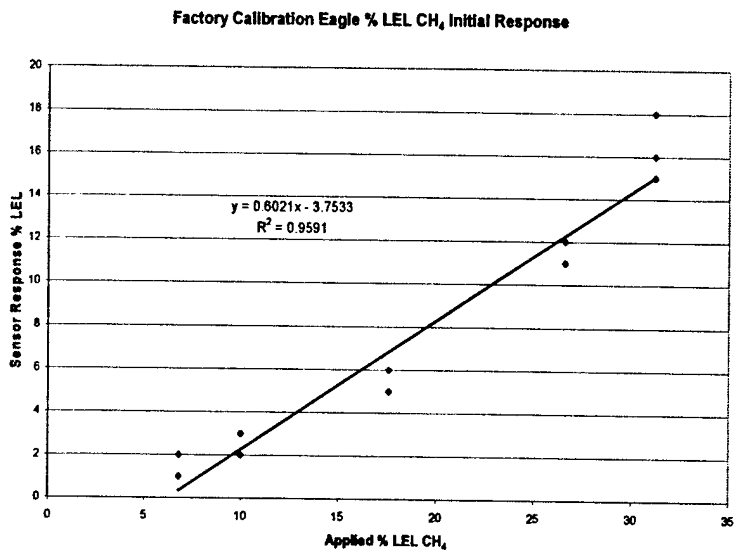

Dräger Post Recalibration $H_2S$ Response
y = 0.9292x + 0.2406
$R^2$ = 0.9992
Sensor Response ppm
Applied ppm $H_2S$


Genesis Post Recalibration $H_2S$ Response
y = 1.2352x - 4.9677
$R^2$ = 0.9975
Sensor Response ppm
Applied ppm $H_2S$

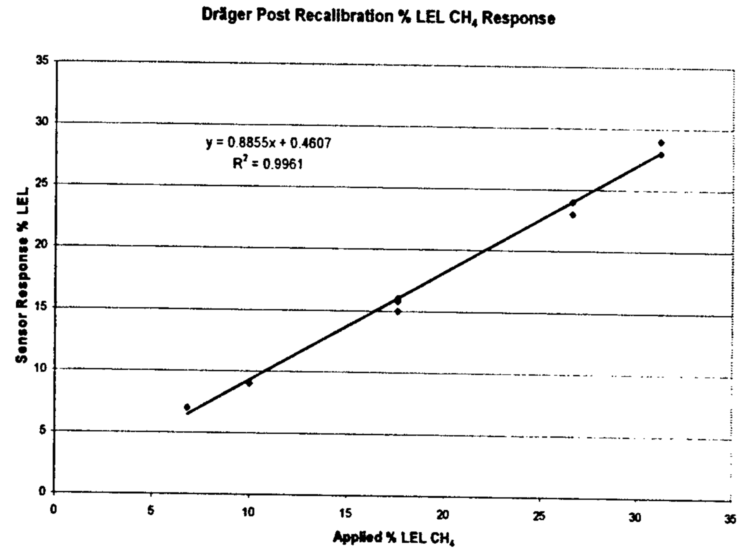

ITX Post Recalibration $H_2S$ Response
y = 0.8002x - 2.1376
$R^2$ = 0.9988
Sensor Response ppm
Applied ppm $H_2S$


Factory Calibration PhD5 $H_2S$ Initial Response
y = 0.7432x - 0.8948
$R^2$ = 0.9961
Sensor Response ppm
Applied ppm $H_2S$

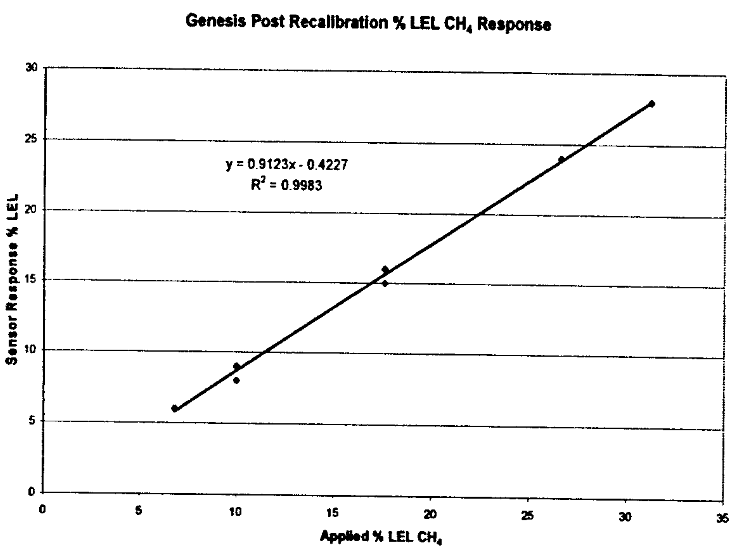

Omni Post Recalibration $H_2S$ Response
y = 0.7327x - 1.3737
$R^2$ = 0.9986
Sensor Response ppm
Applied ppm $H_2S$



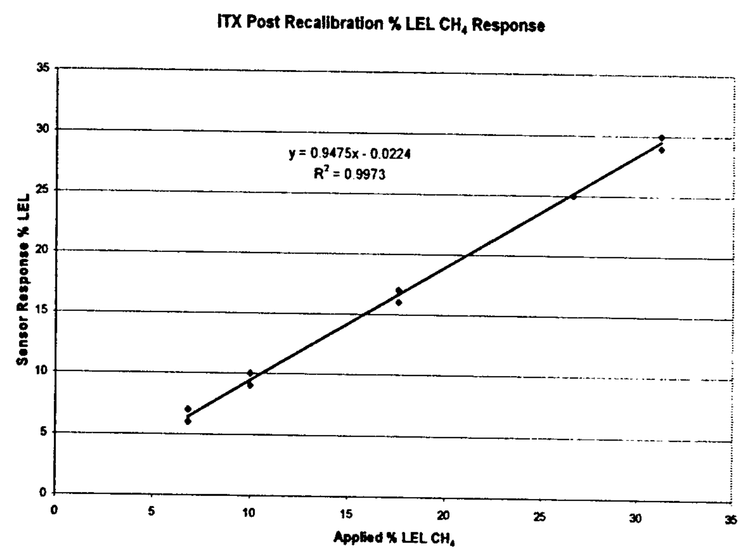
Factory Calibration Eagle % LEL CH4 Initial Response
y = 0.6021x - 3.7533
R² = 0.9591
Sensor Response % LEL
Applied % LEL CH4

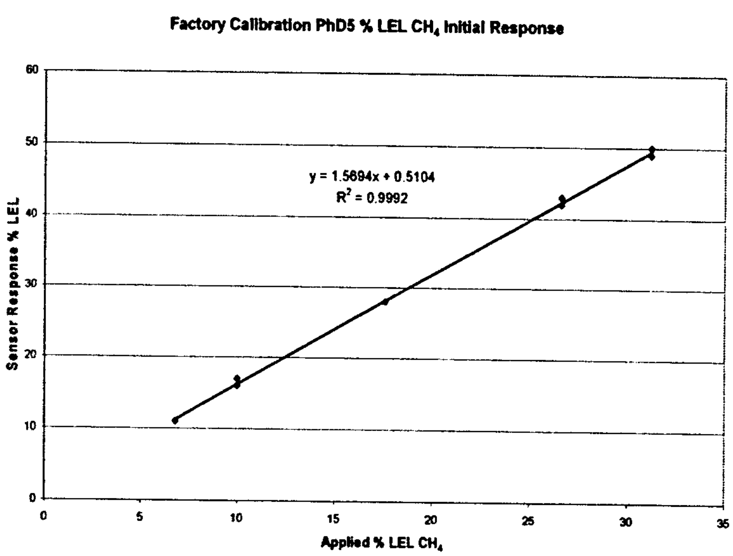
Dräger Post Recalibration % LEL CH4 Response
y = 0.8855x + 0.4607
R² = 0.9961
Sensor Response % LEL
Applied % LEL CH4

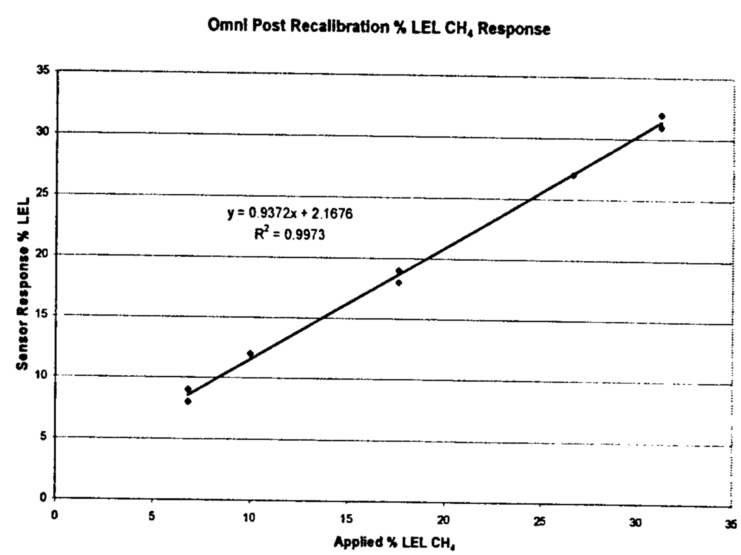
Genesis Post Recalibration % LEL CH4 Response
y = 0.9123x - 0.4227
R² = 0.9983
Sensor Response % LEL
Applied % LEL CH4

ITX Post Recalibration % LEL CH4 Response
y = 0.9475x - 0.0224
R² = 0.9973
Sensor Response % LEL
Applied % LEL CH4

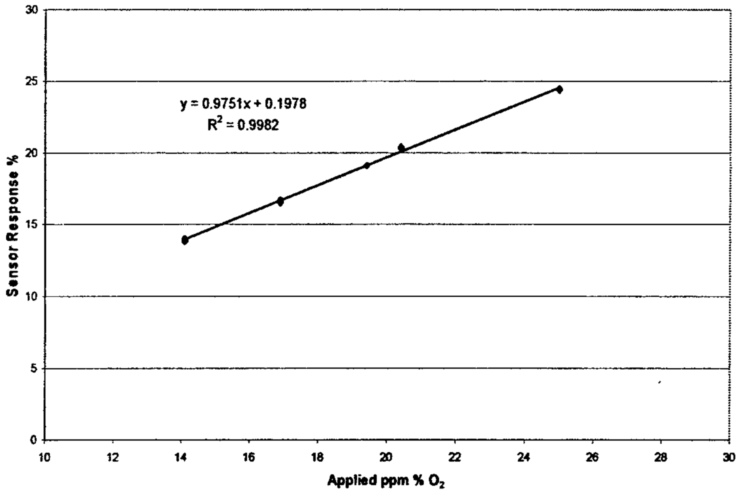



Factory Calibration PhD5 % LEL CH4 Initial Response
y = 1.5694x + 0.5104
R² = 0.9992
Sensor Response % LEL
Applied % LEL CH4

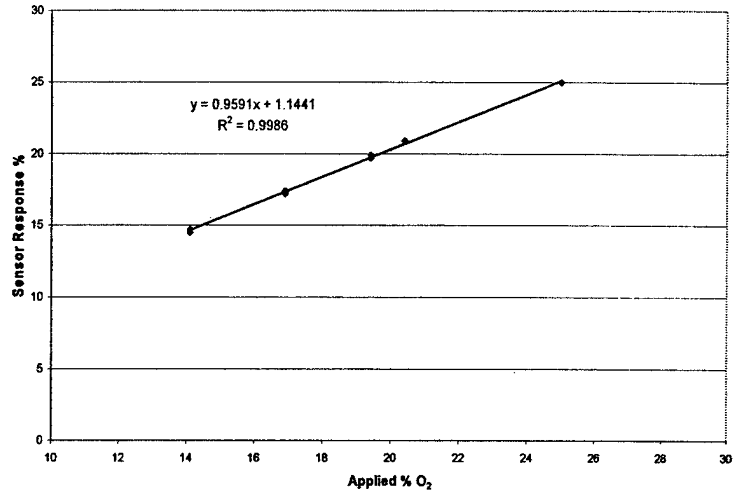



Omni Post Recalibration % LEL CH4 Response
y = 0.9372x + 2.1676
R² = 0.9973
Sensor Response % LEL
Applied % LEL CH4

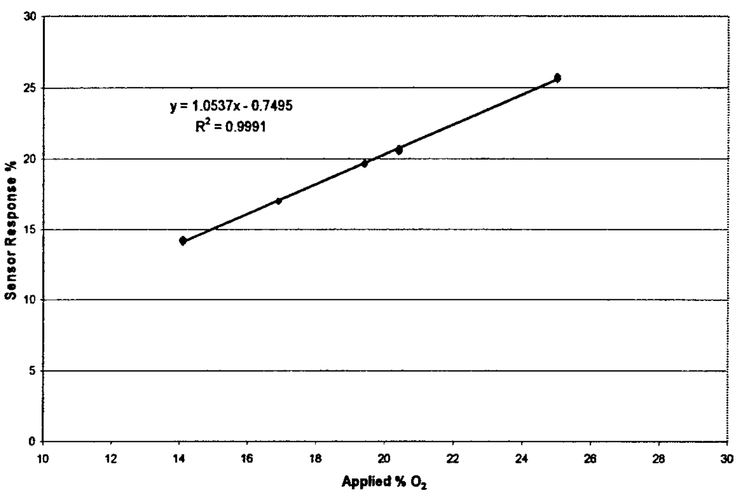
Factory Calibration Eagle $O_2$ Initial Response



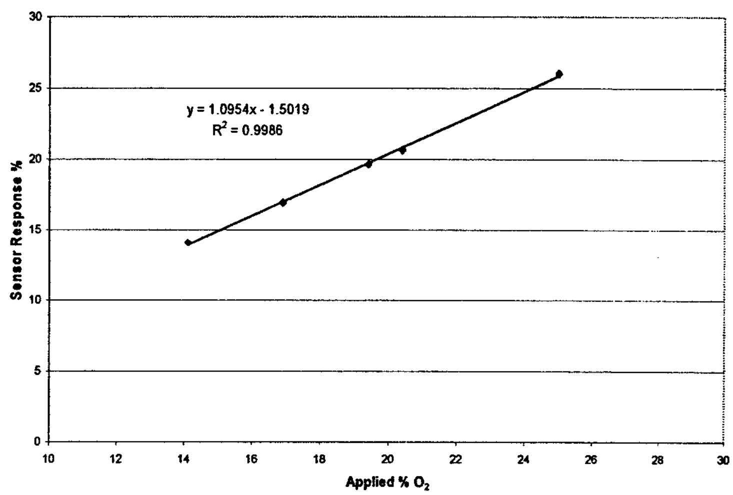

Dräger Post Recalibration $O_2$ Response



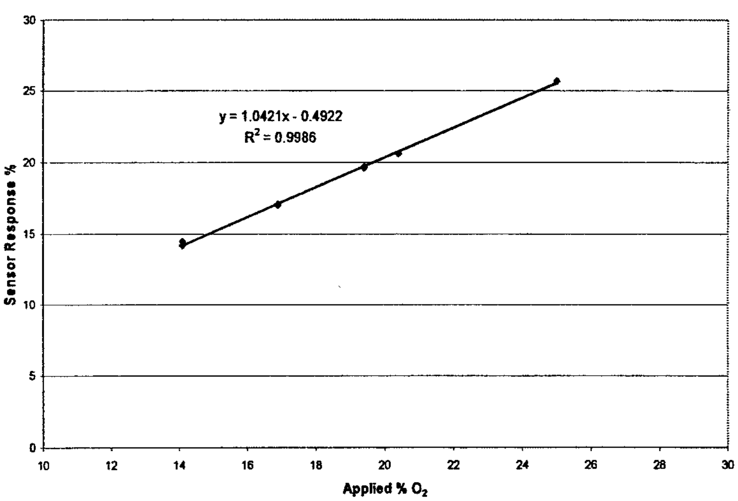

Genesis Post Recalibration $O_2$ Response



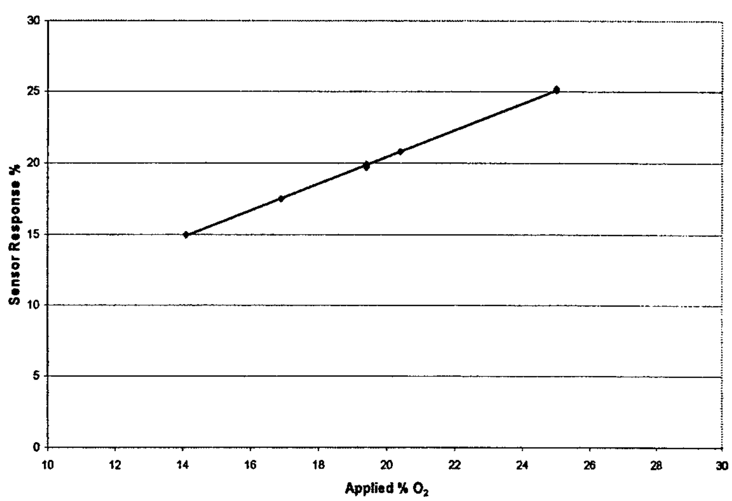

iTX Post Recalibration $O_2$ Response



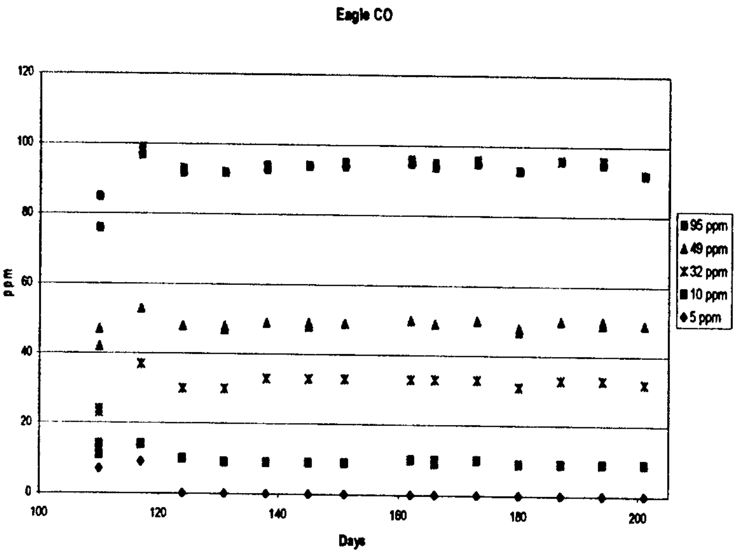

Factory Calibration PhD5 $O_2$ Initial Response



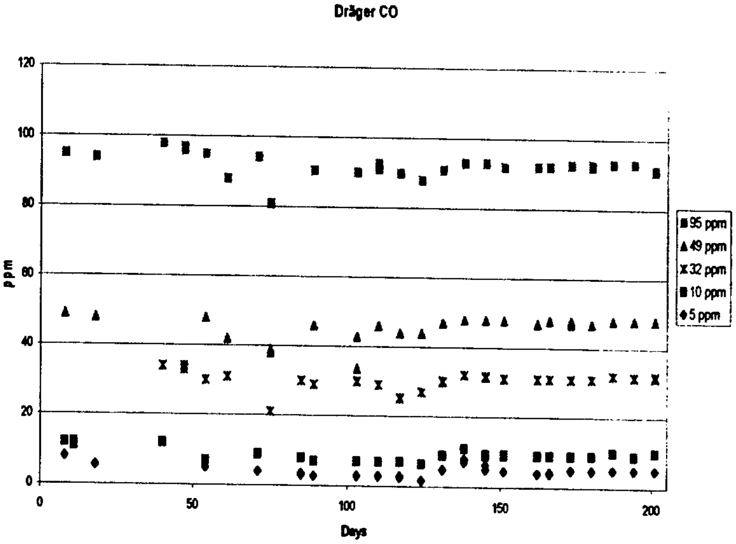

Omni Post Recalibration $O_2$ Response



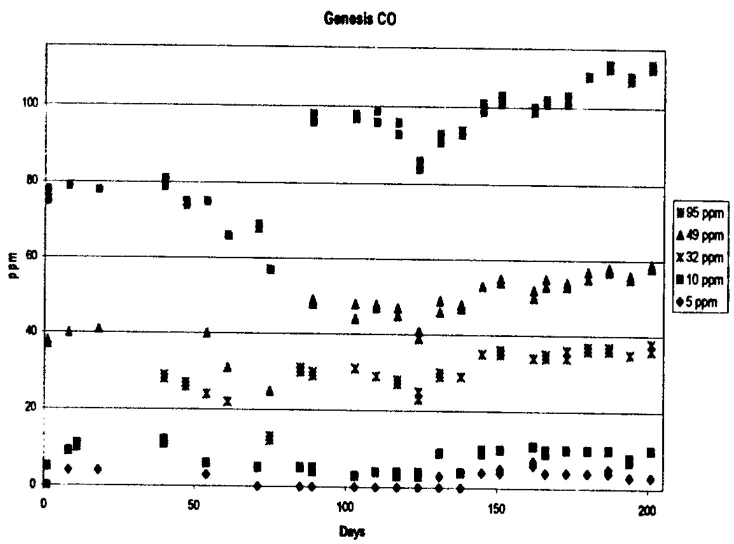
## Appendix C



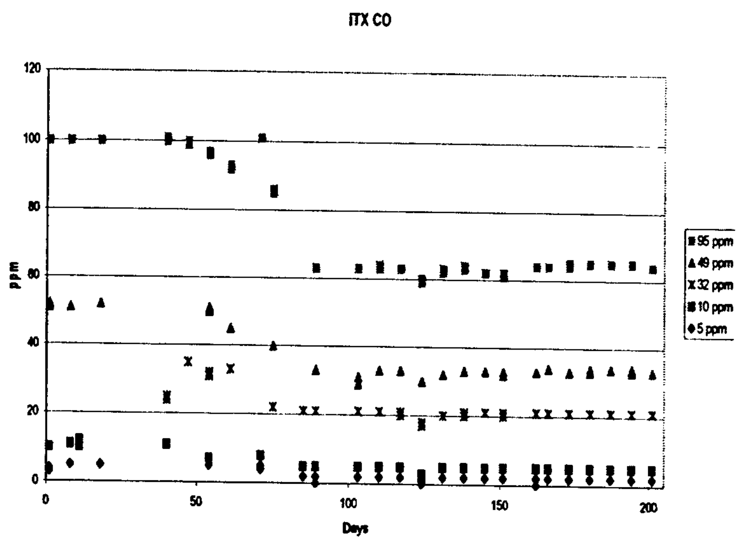
Eagle CO
ppm
Days
95 ppm
49 ppm
32 ppm
10 ppm
5 ppm

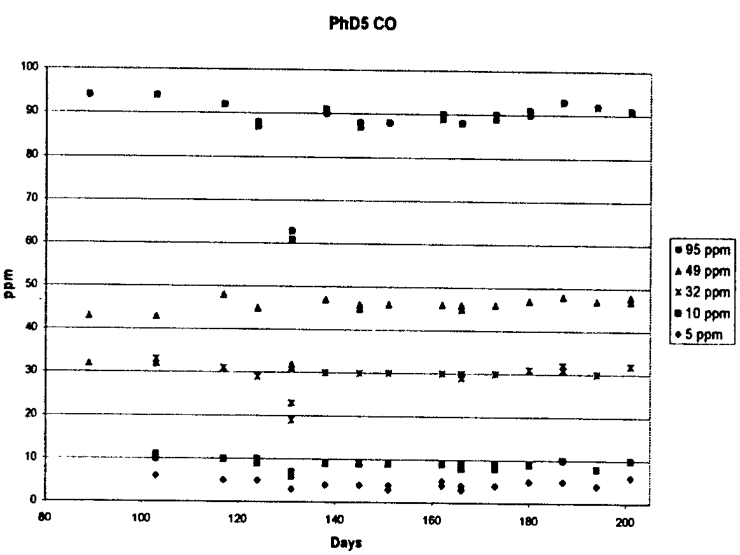
Dräger CO
ppm
Days
95 ppm
49 ppm
32 ppm
10 ppm
5 ppm

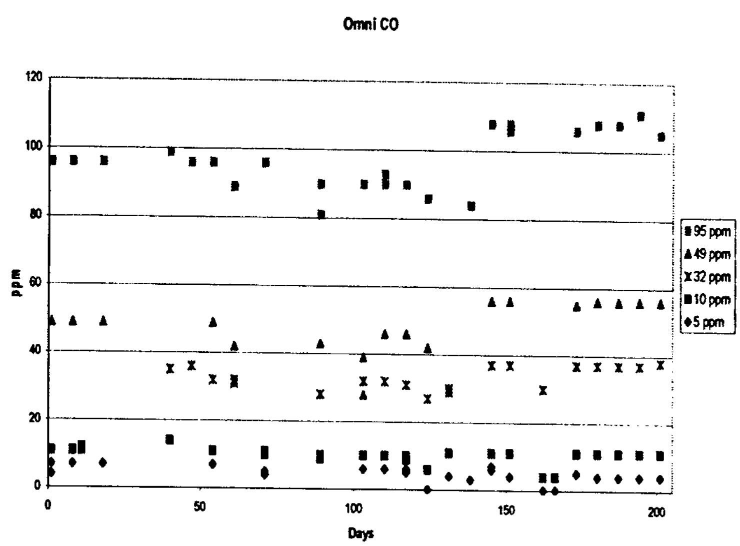
Genesis CO
ppm
Days
95 ppm
49 ppm
32 ppm
10 ppm
5 ppm

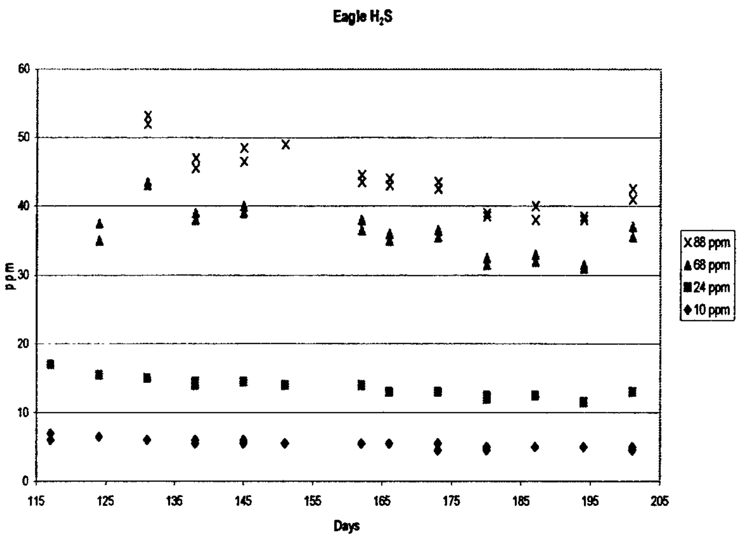
ITX CO
ppm
Days
95 ppm
49 ppm
32 ppm
10 ppm
5 ppm

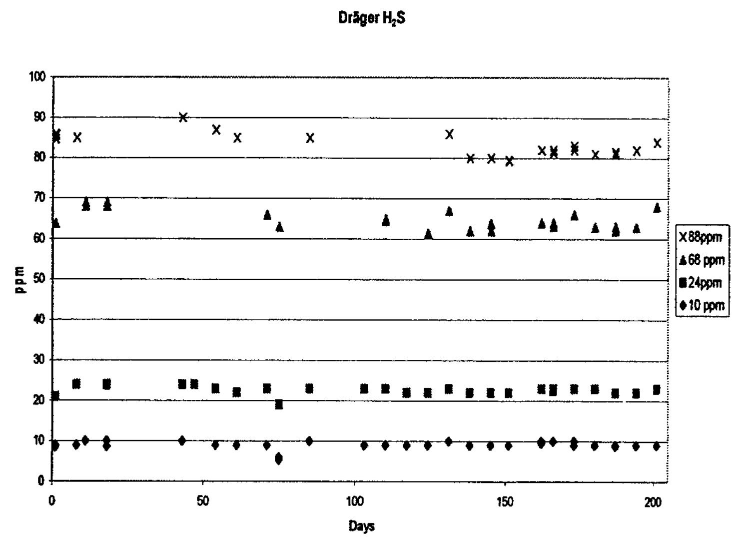



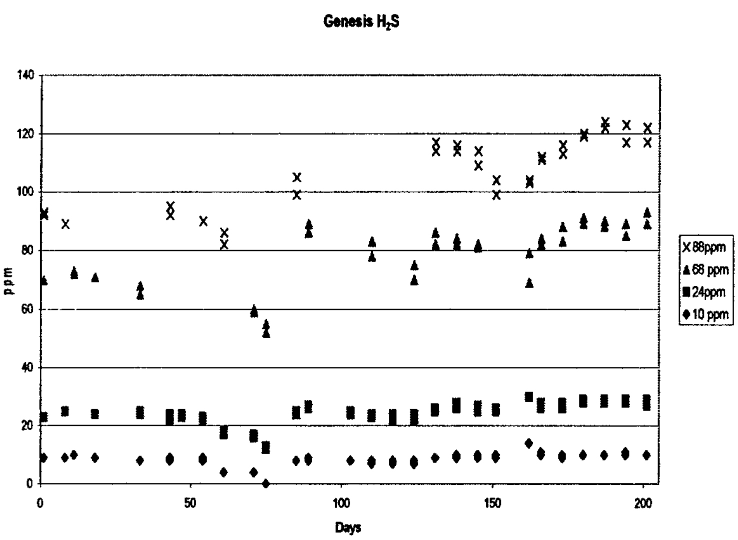
PhD5 CO
ppm
Days
95 ppm
49 ppm
32 ppm
10 ppm
5 ppm

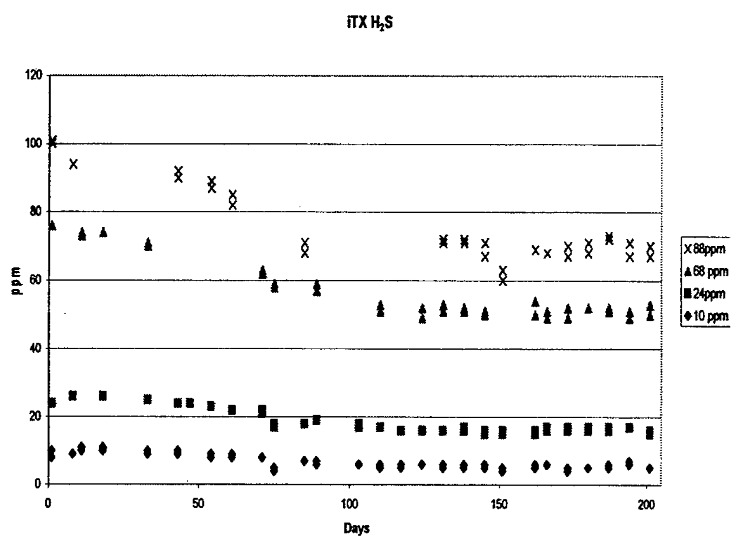



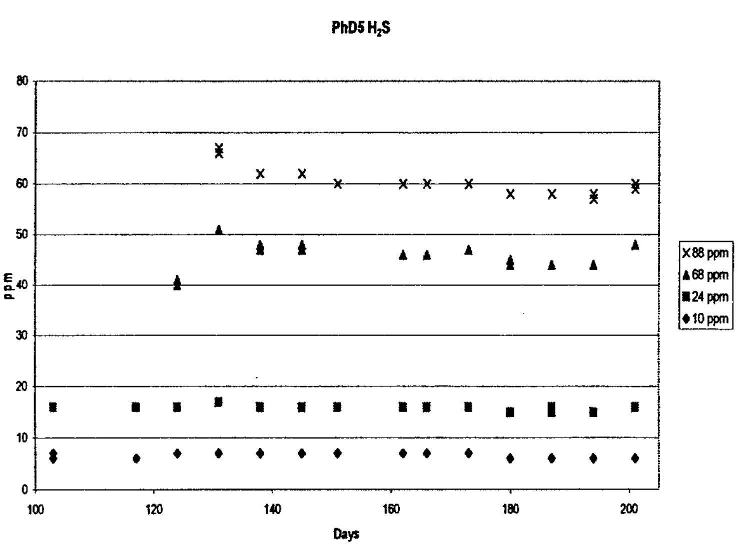
Omni CO
ppm
Days
95 ppm
49 ppm
32 ppm
10 ppm
5 ppm

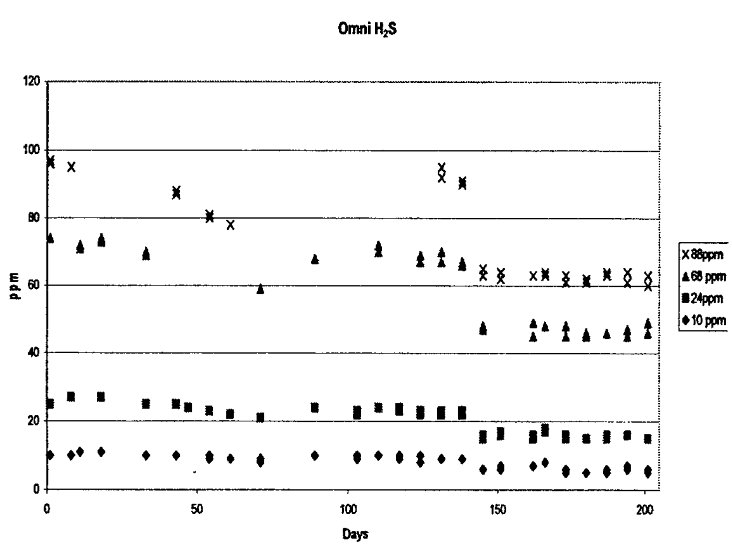

Eagle H2S
ppm
Days
X 88 ppm
▲68 ppm
■24 ppm
◆10 ppm

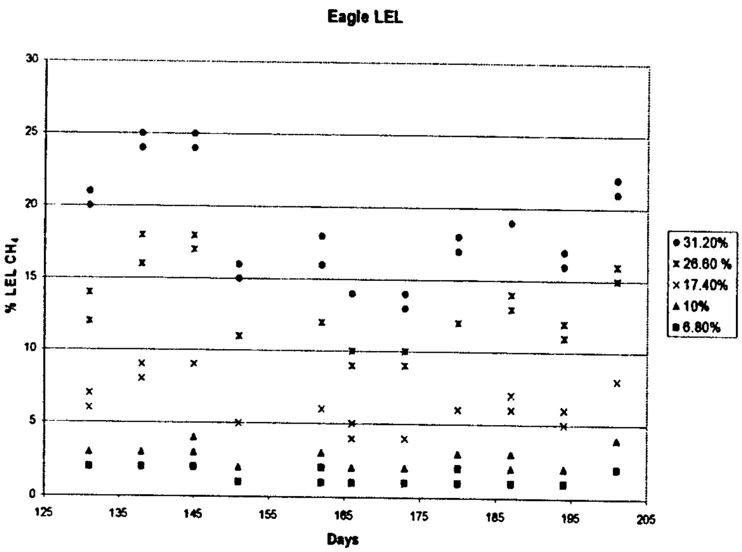

Dräger H2S
ppm
Days
X 88ppm
▲68 ppm
■24ppm
◆10 ppm

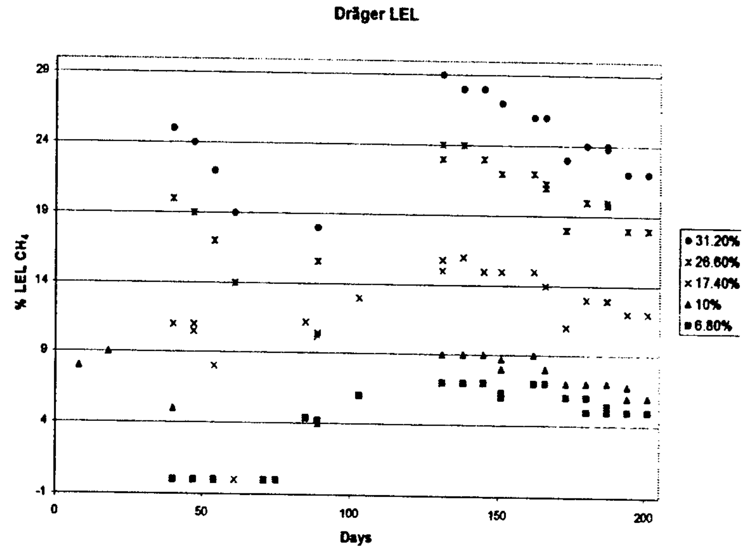

Genesis H2S
ppm
Days
X 88ppm
▲68 ppm
■24ppm
◆10 ppm

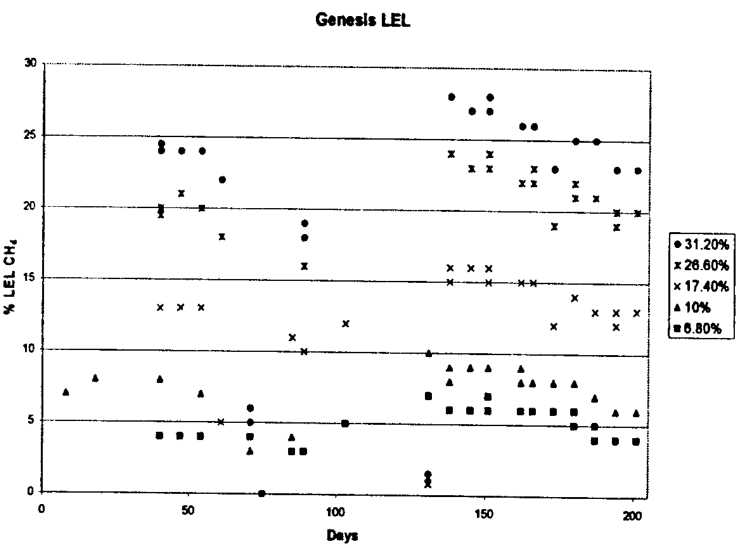

iTX H2S
ppm
Days
X 88ppm
▲68 ppm
■24ppm
◆10 ppm

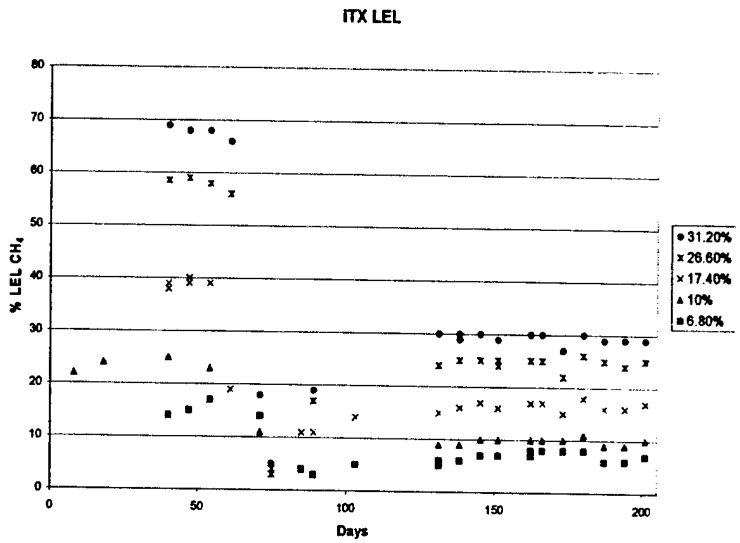

PhD5 H2S
ppm
Days
X 88 ppm
▲68 ppm
■24 ppm
◆10 ppm

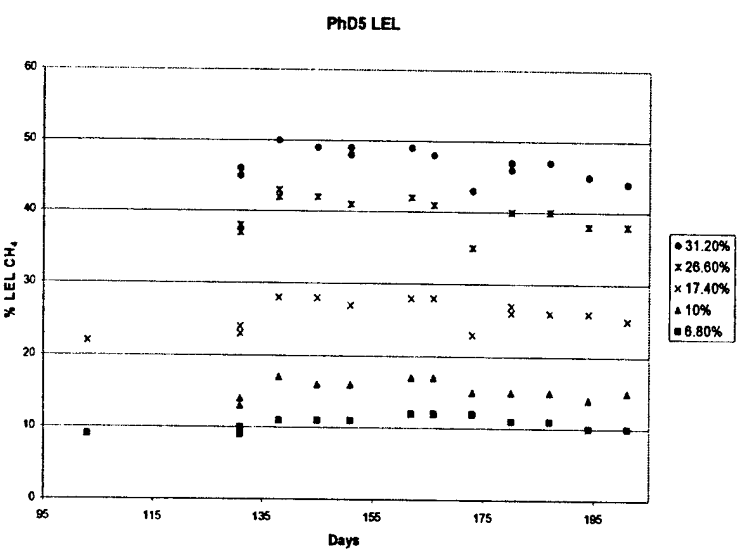

Omni H2S
ppm
Days
X 88ppm
▲68 ppm
■24ppm
◆10 ppm

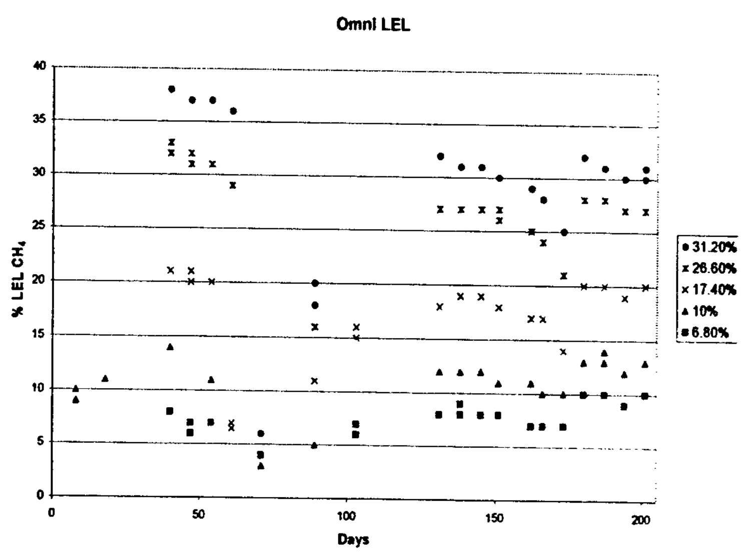

Eagle LEL
% LEL CH4
Days
31.20%
26.60 %
17.40%
10%
6.80%


Dräger LEL
% LEL CH4
Days
31.20%
26.60%
17.40%
10%
6.80%

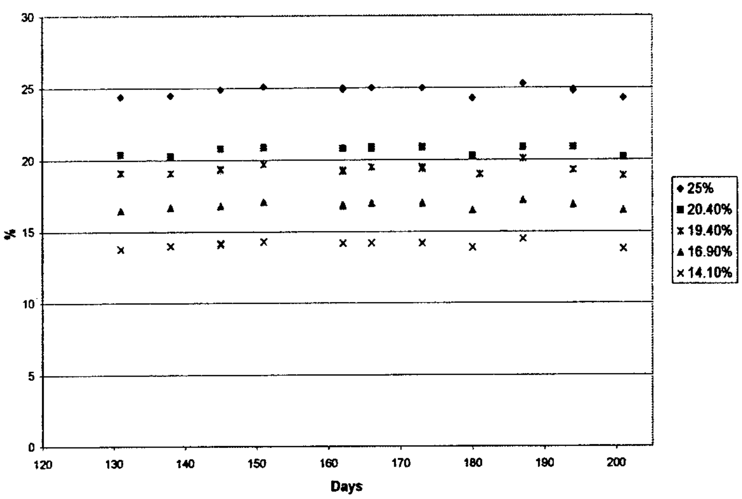

Genesis LEL
% LEL CH4
Days
31.20%
26.60%
17.40%
10%
6.80%


ITX LEL
% LEL CH4
Days
31.20%
26.60%
17.40%
10%
6.80%

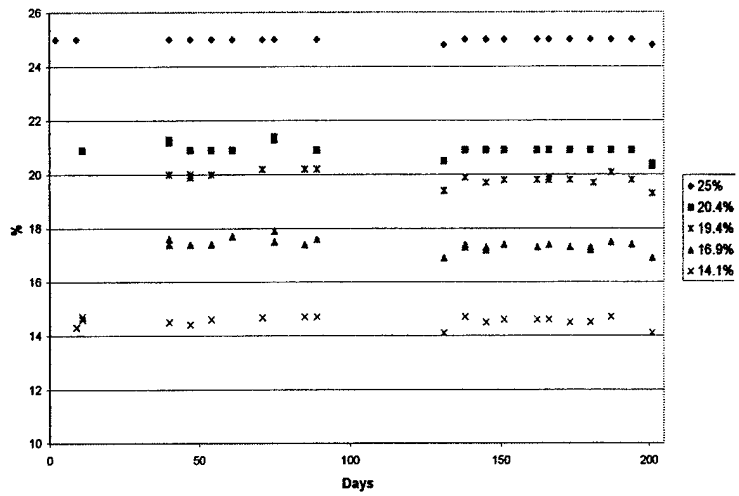

PhD5 LEL
% LEL CH4
Days
31.20%
26.60%
17.40%
10%
6.80%


Omni LEL
% LEL CH4
Days
31.20%
26.60%
17.40%
10%
6.80%

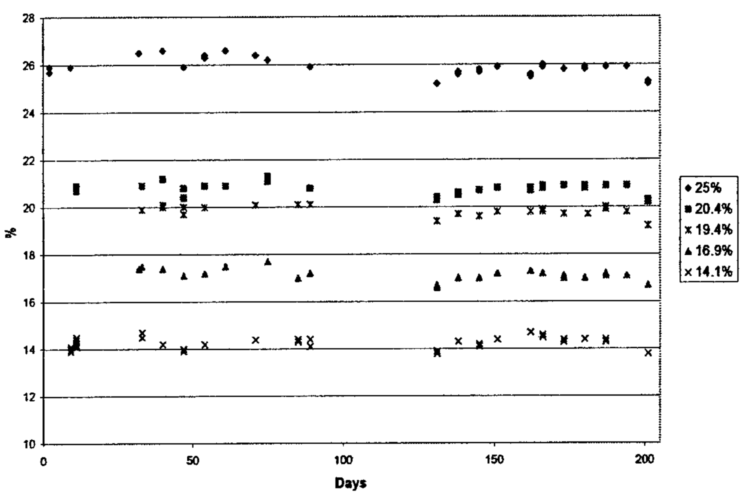
Eagle $O_2$



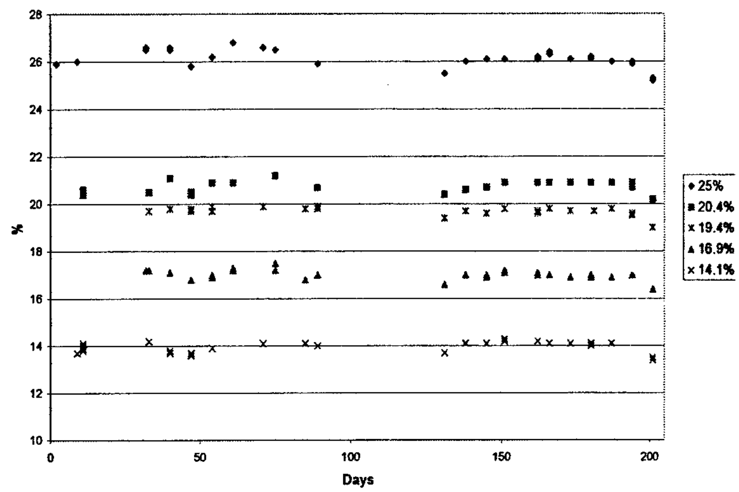

Dräger $O_2$



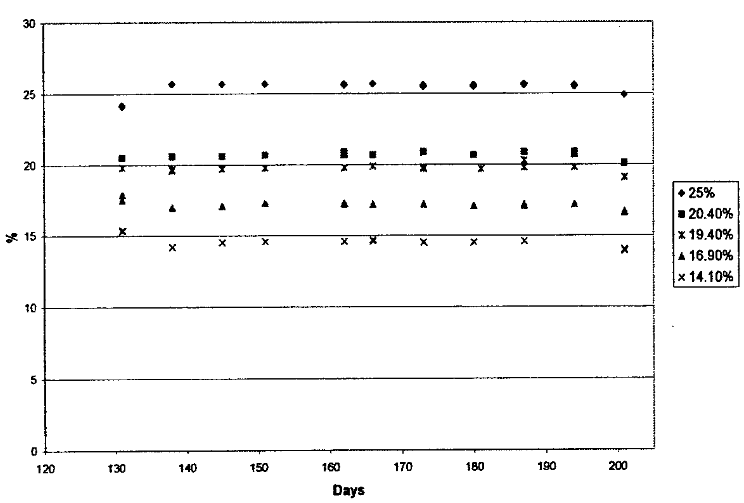

Genesis $O_2$




ITX $O_2$




PhD5 $O_2$




Omni $O_2$